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# BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science

(IZVESTIYA AKADEMY NAUK SSSR)

(OTDELENIE KHIMICHESKIKH)

IN ENGLISH TRANSLATION

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(IZVESTIYA AKADEMII NAUK SSSR  
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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY  
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.- Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

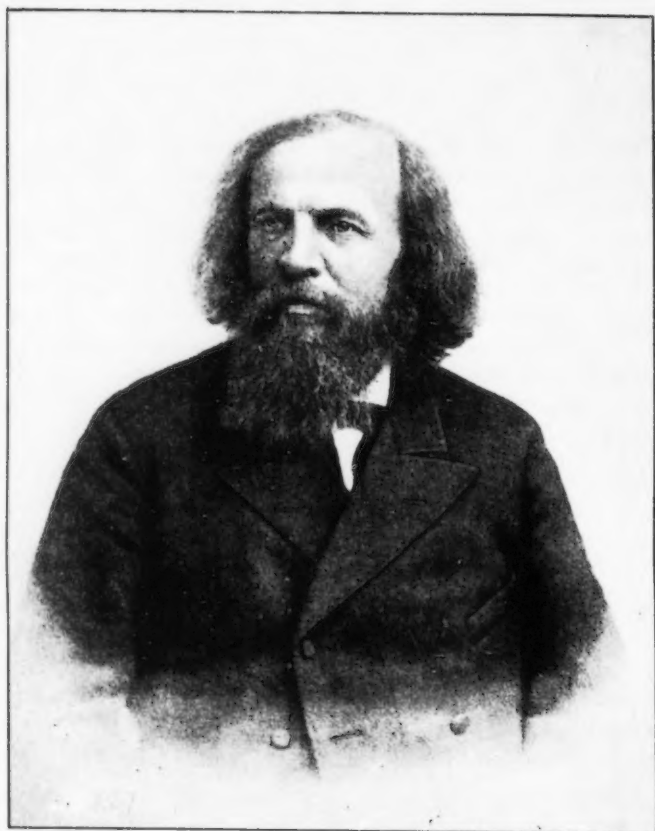
## MENDELEEV AND THE PRESENT STATE OF DEVELOPMENT OF HIS IDEAS

On the Occasion of the Fiftieth Anniversary of his Death (1907-1957)

Fifty years ago, on January 20 (February 2, New Style), 1907, science suffered an irretrievable loss in the person of the world-renowned scientist, the great Russian chemist, Dmitry Ivanovich Mendeleev. This great loss cast a dark shadow over a year which might have become one of the brightest in the progressing course of culture. In fact, it was in 1906-1907 that Einstein published the principle of the equivalence of mass and energy, which followed from the theory of relativity that he had only just discovered. Nernst announced his third law of thermodynamics. Landolt and Emil Fischer completed important investigations that had occupied them for many years—the former on the precise verification of the fundamental Lomonosov law of the conservation of matter, and the latter on the synthesis of polypeptides. Otto Hahn discovered protoactinium. Willstätter established the structure of chlorophyll, and many other monumental scientific discoveries were announced. At the same time, however, joy in the increased knowledge of and power over nature was clouded by a series of sad events. Relentless death carried away the lives of scientists whose bold creative ideas had for years led other scientists forward: Berthelot, Moissan, Pierre Curie, Roozeboom, Boltzmann, Nikolai Menshutkin, and finally D. I. Mendeleev. It was indeed a grievous year in the history of science!

The most severe of these losses was that of D. I. Mendeleev. "Newton, Kepler, Darwin, and Marx, and to these we must now add Mendeleev—as personified in their theoretical conclusions, they constitute a precious heritage for all thinking mankind," wrote the scientist and revolutionary N. A. Morozov in this same year, "Their discoveries lie at the foundation of the world-view of each one of us, and they will lie at the foundation of the world-views of future generations. That is why not only men of science, but also young students and people representative of every possible kind of human activity followed the remains of Mendeleev in the long procession which proceeded on January 27, 1907, from the Technological Institute to the Volkovo cemetery, where he was buried alongside Dobrolyubov, Pisarev, Turgenev and other great writers and scientists of our country"... "And I believe that the time is not far distant when a liberated Russia will raise monuments in its squares not only to those who fought for its civic freedom, but also to those who fought for freedom of thought—and among these monuments there will be one to the memory of Dmitry Ivanovich Mendeleev."

At the end of the same year—December 19, 1907—the first Mendeleev Congress was called in St. Petersburg by the Russian Physical and Chemical Society. The most prominent Russian chemists took part, and through their scientific addresses they honored the great name of the founder of the Russian Chemical Society. N. N. Beketov was elected president of the Congress, F. M. Flavitsky, N. E. Zhukovsky, P. N. Lebedev, P. I. Walden, I. A. Kablukov, S. N. Reformatsky, D. N. Pryanishnikov, and S. Arrhenius were elected vice-presidents, and L. A. Chugaev and N. P. Kosterin were appointed secretaries. Papers were read by V. E. Tishchenko on the biography of Mendeleev, by N. N. Beketov on the significance of the periodic system, by G. G. Gustavson on D. I. Mendeleev and organic chemistry, by P. I. Walden on his investigations on the theory of solutions, by B. P. Veinberg on his investigations on molecular physics, by F. Ya. Kapustin on the changes in the volumes of gases and liquids, by N. E. Zhukovsky on his investigations on the resistance of liquids and on aeronautics, by A. I. Voelkov on his investigations on meteorology, by V. Kharichkov on the study of petroleum, by N. P. Rubtsov on the study of explosives, by N. G. Egorov on metrology, and by V. Ya. Kurbatov, who gave a general review of the activities of the great scientist. Thus, in twelve papers by students, colleagues, and followers of D. I. Mendeleev, the great variety of work carried out by the great chemist and physicist was reviewed and summarized; in the course of his life he published more than five hundred papers. Both the first, and also the succeeding Mendeleev Congresses were devoted to reviews of scientific progress. At the same 1907 Congress, a group of Moscow





members of the Russian Physical and Chemical Society — N. D. Zelinsky, L. A. Chugaev, V. P. Pavlov, and I. A. Kablukov — presented a written report which proposed the creation of a D. I. Mendeleev Chemical Institute. The Congress unanimously adopted this proposal, which has not yet been realized.\*

The fruits of the scientific creativeness of D. I. Mendeleev belong in equal measure to all countries, all peoples, and all times. But he himself was truly a Russian scientist, constantly concerned for the well-being of his homeland and for its cultural progress: he was indeed a worthy representative of his Fatherland. Like his great predecessor, M. V. Lomonosov, Mendeleev often lent emphasis to this in his utterances, and even within a relatively short time of his death (1896), writing in reply to chemists assembled together on the occasion of the jubilee of the University of St. Petersburg, he stated: "I greatly regret that it is beyond my strength to take my place with my fellow chemists, but I believe that they will act in our country's interest, as the now decrepit D. Mendeleev used to try to do."

\* \* \*

D. I. Mendeleev was born on January 27 (February 8, New Style), 1834, in Tobolsk, Siberia. He passed from high school to the St. Petersburg Main Pedagogic Institute (1850), where he attended lectures on chemistry by A. A. Voskresensky, on mathematics by M. V. Ostrogradsky, on physics by E. Lenz, and on mineralogy by S. S. Kutorga.

After leaving the Institute with a gold medal, Mendeleev served in the Simferopol (1855) and First Odessa High Schools. A year later he passed an examination in St. Petersburg University and defended a thesis on "Specific Volumes" for the degree of Master. He also defended a thesis on "The Structure of Silicon Compounds" and obtained the title of Assistant Professor. At the age of twenty-three he began to teach chemistry, and he continued to do so for thirty-four years. In 1859-1861 Mendeleev went on a scientific mission and visited Heidelberg, where he attended lectures by Kopp, Bunsen and Kirchhoff; it was here, in the course of work in his private laboratory, that he discovered the existence of the critical temperature.

On his return to St. Petersburg, Mendeleev wrote the first textbook of organic chemistry in the Russian language, and for this he received the Demidov Prize from the Academy of Sciences. After being appointed professor of the St. Petersburg Practical Technological Institute (1864), Mendeleev defended his doctorate thesis on "The Compound formed by Alcohol with Water" (1865) and was appointed Ordinary Professor of the University in technical chemistry and later (1867) also in inorganic chemistry. Mendeleev then began work on the course of lectures that led to the discovery of the periodic law and the periodic system of elements (1869) and to the writing of "The Principles of Chemistry." At about this time (1868) Mendeleev began to take part in the organization of the Russian Chemical Society, which was named after him after the Revolution. In 1890 Mendeleev was compelled to leave teaching and he was appointed to the post of scientist-keeper at the Depot of Standard Weights and Measures, an organization which later (1893) became the Board of Measures and Weights (and still later the Mendeleev All-Union Institute of Metrology). In 1907, while still at this post, Mendeleev died of pneumonia.

Coming, as he did, before his time, Mendeleev was a scientist and innovator who could never reconcile himself with the routine and conservatism of tsarist Russia. He was personally acquainted with I. M. Sechenov and N. A. Dobrolyubov, he studied the works of A. I. Gertsen and Marx, he read the "Kolokol," and he was at loggerheads with the proponents of spiritualism: he was unable to act as a "yes man" for the representatives of the official regime. For example, he agreed to present a students' petition to a minister, Count Delyanov, and it was returned to him with a resolution that he found insulting; this stated that "neither the minister nor anyone in his Imperial Majesty's service has the right to accept documents of this sort," and it prompted Mendeleev to hand in his resignation. Still earlier an event occurred in which the governing cliques of the tsarist regime exerted their influence in a decisive way. Having been elected a corresponding member of the Academy of Sciences in 1876, Mendeleev was later (1880) proposed by A. M. Butlerov for election as a full

\* More correctly, it has been realized only partially: namely, by the creation after the Revolution of the Mendeleev Institute in Moscow, but only as a higher educational establishment.

member, but the voting did not go in his favor and there was a storm of indignation throughout Russia.

The full list of Mendeleev's titles and degrees is extremely long: he was an honorary doctor and member of more than one hundred (1) scientific institutes, societies, and academies throughout the world. For this reason, his "nonelection" as a Russian academician was all the more insulting.

A short list of the main facts of the biography of Mendeleev gives no idea of the nature of the activities of this great scientist, of his life, and of his scientific creativeness. We must now discuss these matters, and wherever possible we shall examine also the development of his creative ideas right down to the present day. But to present a review of all his researches—even without pretense to exhaustiveness, and even in the form of a fragmental account of purely illustrative character—is impossible in a short article. We therefore confine ourselves to an extremely concise review of the three lines of Mendeleev's work that are undoubtedly of the greatest importance: those associated with the periodic law, with the theory of solutions and with industry and agriculture.

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One of the greatest discoveries of the nineteenth century—a discovery which brought about a veritable revolution in chemistry—was the discovery of the periodic law of the elements by D. I. Mendeleev in 1869. The periodic law, according to which the properties of the atoms of the elements, and particularly their chemical properties, bear a periodic relationship to their atomic weights, has not undergone any changes in principle during the last 88 years: we may note only that, after the investigations of Moseley (1913), the atomic weight, as a characteristic of the individual nature of an element, was replaced by the charge of the atomic nucleus. The system of elements based on Mendeleev's law introduced strict and rational systematization of all the elements into our science for the first time. Chemistry not only acquired a fundamental theoretical generalization, and not only became a science whose regular and majestic structure derived from a single principle, but acquired also a reliable and well-tried tool—a method of predicting new facts and generalizations.

As is well known, on the basis of the periodic system Mendeleev himself predicted the existence and properties of three unknown elements corresponding to unoccupied places in the system, and these predictions were very soon fulfilled; there followed the discoveries of gallium (Lecoq de Boisbaudran, 1875), scandium (Nilson and Cleve, 1879), and germanium (Winkler, 1886). As W. Ramsay testified, in the discovery of the inert gases Mendeleev's law again formed the most important guide in the investigation. These brilliant proofs of the value of the periodic law produced a great impression throughout the world, and the historian of chemistry, Jaffe, wrote "All the world came knocking at the door of the Russian in St. Petersburg." With Mendeleev's death the search for and investigations of new elements carried on with ever increasing intensity along the paths that he had marked out. The "dvi-manganese" that he predicted, the element of atomic number 75, was discovered in 1925 by the Noddacks and named by them rhenium. Of particular interest was the work on "synthetic" elements, namely the transuranides, from neptunium (atomic number 93) to mendelevium (atomic number 101), which was carried out in the light of Mendeleev's law in 1945-1955. All these elements, which were discovered by McMillan, Seaborg and others and are so important for the problem of the utilization of atomic energy, found their place in the periodic system, which served as a powerful means of predicting their properties and an aid in the further study of their chemistry.

The Mendeleev periodic law provided a valuable instrument in the creation of the modern theory of the structure of matter. The law made possible the discovery of the Pauli principle, which asserts the impossibility of the existence of two identical electrons in an atom; it made possible the introduction of the concept of the layered electronic structure of atoms, of the stability of an "octet" of electrons, and of the formation of chemical bonds as a result of the transition of electrons from atom to atom. Both the static and dynamic atomic models of G. N. Lewis and W. Kossel (1902-1916) are derived from the periodic law. At the same stage the mutually productive effects of spectroscopy and the periodic system led to the discovery of the new element hafnium by Coster and Hevesy (1922). Already at this stage of the development of science it was possible to state boldly that the periodic law had become the principal medium in the creation of the modern theory of the structure of atoms and molecules and in the theory of the chemical bond. By this very fact, the periodic law of the elements became a factor of exceptional importance also in the further confirmation and

development of the philosophy that determines our whole comprehension of the world, the philosophy of dialectical materialism— as was noted for the first time in the last century by F. Engels in his work "The Dialectics of Nature."

The development of Mendeleev's ideas on the periodic law has proceeded mainly in two directions: further improvement in the actual form in which the system is drawn up, and the discovery of new periodically varying properties of atoms. As regards the first direction, we must mention, in particular, two investigations that have found extensive application over several decades. Having proposed his theory of atomic structure, Niels Bohr drew up a scheme for the system of elements classified according to the structures of their electron envelopes. This "step" or "ladder" form, which emphasizes the relation of the Mendeleev law to the fundamentals of the theory of the structure of matter, was proposed also by Thomsen at about the same time and has since been known to science as the Bohr-Thomsen system. Still earlier (1905) Alfred Werner had proposed the use of the so-called "long" variant of the system, which is convenient for the description of many properties, particularly in the chemistry of complex compounds.

Both these methods of representation had already been anticipated by Mendeleev himself; Bohr and Thomsen only repeated in a more detailed form the vertical variant, which was one of the first examined by Mendeleev, and he had previously given also the "long-period" Werner variant. However, the author of the periodic system had long found that the most generally useful and convenient form was the horizontal variant which has been so extensively used right up to the present time.

Nevertheless, numerous attempts to find new forms for expressing the periodic law have continued throughout this half-century. As they appeared they were reported in the review articles and monographs on Mendeleev's discovery which were written by L. A. Chugaev (1913), V. Ya. Kurbatov (1925), E. Rabinovich and E. Tilo (1933), and others. Summaries of this work were published in connection with Mendeleev Congresses (1927 and 1934-1936). All sorts of representations on a plane and in space were used, but they were all one-sided in application and had what we may call a "particular" character as compared with the fundamental representation of the system of Mendeleev himself. Articles on these matters continue to appear. Among these we may single out the work of the British chemist Tomkeieff (1954), who proposed screw, conical and spiral projections of representations of the system in which the principle of the latitude-longitude network of cartography was used and which are convenient for the representation of various properties, for example the densities of the elements; there is also the table published in 1954 by Mendoza, professor at the Peru University, Cuzco, which consists of 1100 cells and permits the systematization of the various combinations of protons and neutrons as ingredients of the nuclei of the various elements.

Among these investigations particular reference must be made to work on the place occupied by the transuranic elements. An important step was made by Seaborg (1953) when he proposed that these elements should be regarded as analogs of the rare-earth elements and should be considered, as the family of actinides, in their relation to the family of lanthanides (actinoids and lanthanoids, according to S. A. Shchukarev). Although Seaborg's proposal cannot yet be regarded as generally accepted and it is in some respects controversial, it is continually gaining greater acceptance.

Appreciable progress has been made in the direction of recognizing atomic nuclei as structures which also show a periodic behavior and so correspond to a new expression of the periodic law. Although chemists (for example the author in 1954) have made some attempts to classify the existing material, we shall not discuss the matter here, since it is mainly the concern of theoretical physics. We must, however, point out the importance of this line of work.

We will turn now to the discovery of new, previously unstudied, periodically varying properties of the atoms of chemical elements. In the course of the last fifty years it has been found possible to establish the conformity of many properties of elements and simple species to the Mendeleev system. Investigation of this question not only supplemented the number of illustrations of the manifestation of the great law of nature, but aided in the closer study of the actual course of changes within the limits of the system and so in the discovery of various new, previously unknown laws. A good example is the discovery of E. V. Biron (1915) of a secondary periodicity, shown in a more or less periodic variation of certain properties within the limits of each group. It is interesting that several new physicochemical characteristics of atoms and ions which have been recently introduced into science also show clear conformity to the Mendeleev law.

Ionic radii, as established by W. Goldschmidt in 1926, are in complete conformity with the periodic system. The same can be said of ionic potentials (Cartledge, 1928), electronegativities of atoms (Pauling, 1932), and electronegativities— or strictly speaking, crystallochemical electronegativities— of ions (the author, 1949). It is now clear that, as the periodicity of the properties of atoms is linked in a most direct fashion with the periodicity in the structures of their electron envelopes, any property that depends in any way on the structure of the electron envelope will also show periodic variations.

It will be obvious from the above that the most significant item of our heritage from Mendeleev — the periodic law — has been long incorporated in world science and has been intensively developed in all countries of the world. In this work a great part has been played by Mendeleev's fellow countrymen — or, in our time, the school of Soviet chemists. The former included N. A. Morozov, F. M. Flavitsky and E. V. Biron, and the latter includes, among many others, A. E. Fersman, S. A. Shchukarev, E. V. Akhumov, V. I. Spitsyn, and I. P. Selinov. We will cite here only a few illustrative examples. Thus, B. V. Nekrasov gave a more accurate arrangement of elements in the system on the basis of atoms and ions as electronic analogs (according to the structures of the outer electron shells). G. B. Bokiy gave a representation of the system based on the crystallography of the elements. A. N. Nesmeyanov, in the course of extensive researches on the chemistry of heteroorganic (organometallic, etc.) compounds, planned the development of a system in which the data of organic chemistry were included. In our country, mainly by the efforts of V. I. Vernadsky and A. E. Fersman, we created the "chemistry of the earth," or geochemistry, at the basis of which Mendeleev's periodic law was placed. Even in a field which would appear to be far from Mendeleevian ideas, namely thermodynamics, new generalizations were found; the author has shown that the absolute entropies of elements and ions conform completely with the periodic law of the elements.

In the development of nuclear chemistry, an important part has been played by the chemistry of isotopes. S. A. Shchukarev published several papers on generalizations relating to the distribution of the isotopes in the Mendeleev system and the establishment of a periodicity in the variation of the atomic weights themselves with variation of atomic number; he proposed also an explanation for secondary periodicity. On the basis of the theory of numbers and physicochemical analysis, the author made an attempt at the rational construction of the periodic system, and he later indicated the limits of its applicability in regions of superhigh pressures.

The great torch of knowledge — Mendeleev's periodic law — has been found to be a never-failing guide to new discoveries and to be a fundamental law of modern chemistry.

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Throughout practically the whole of his active career, Mendeleev concentrated his attention on the investigation of solutions, which occupied him for about forty years (1864-1906). There was no other problem, not even the periodic law, to which Mendeleev devoted so much attention and on which he worked so long and assiduously in his laboratory. His Master's thesis "Specific Volumes," his doctorate thesis "The Compound formed by Alcohol with Water," his course on "Solutions," which he published in 1875, and his excellent treatise "Investigation of Aqueous Solutions by Density Determination" — such were the milestones marking out Mendeleev's progress in this important field of physical chemistry; in his Collected Works (1934-1937), two volumes (III and IV) were devoted to this work. How can all this be explained? There were two motives: first, a fundamental interest in chemistry, because by a study of solutions Mendeleev hoped to obtain a new understanding of the nature of chemical species; second, he clearly saw the practical value of a study of this field and even set himself the task of "providing reliable data that can be used in practice for the determination of composition from densities."

As a result of investigations over many years, Mendeleev became convinced that "solutions are chemical compounds formed by forces acting between solvent and solute," and he imagined dissociation systems formed by solvent molecules, solute molecules, and definite unstable compounds formed between solvent and solute. These ideas of Mendeleev formed the basis of the hydration, or speaking in general, solvation theory, in the development of which the work of the American scientist Jones played a considerable part.

Mendeleev's chemical theory of solutions was first received rather coldly by most chemists, and some chemists were actively opposed to it. Even at the turn of the century, in 1900, i.e., while Mendeleev was still alive, W. Nernst wrote in his widely read book entitled "Theoretical Chemistry from the Point of View of Avogadro's Hypothesis and Thermodynamics": "The views of Mendeleev — referred to by his followers as the



'hydrate theory of solutions'— have been frequently reiterated recently in spite of the fact that there is as yet no evidence that would give them the right to be called a 'theory of solutions'."

One of the reasons for the sceptical attitude was the absence of simple, mathematically formulated laws describing the principles of the theory. A much more favorable position was occupied by the theory of van't Hoff and Arrhenius—the physical theory of solutions based on an analogy between the gaseous and dissolved states and yielding a series of simple equations, derived thermodynamically, which were found to constitute a good working tool in the investigation of solutions. This theory, which completely ignores interaction between solute and solvent, was directly opposed to the chemical theory. However, this antithesis between the van't Hoff-Arrhenius physical theory and the Mendeleev chemical theory was only temporary. After I. A. Kablukov had published a paper in 1891 in which he laid down the basis of the concept of the hydration of ions, the apparently irresolvable contradictions between the two theories disappeared. There are very many investigations on the modern physicochemical theory of solutions which make extensive use of Mendeleev's idea of interaction between solute and solvent: among many others there are the investigations of V. A. Plotnikov, E. N. Gapon, V. Latimer, K. P. Mishchenko, V. K. Semenchenko and the author.

Of no less importance to science has become the actual method of establishing the existence of compounds in an equilibrium system, by the use of which Mendeleev was able to find support for his views. We are here concerned with the detection of the formation of new chemical individuals from the appearance of special points on the curves of composition-property diagrams. Developing the Mendeleev method, N. S. Kurnakov worked out a general theory of the composition-property diagram which combined chemistry and geometry—so-called physicochemical analysis: this made it possible to establish the amount, nature, and limits of existence of a compound formed in a system consisting of various substances by investigating the changes in properties resulting from change in composition, and then studying the phase diagrams constructed from these data. Very much was done in this direction by N. S. Kurnakov himself and his school. It was thus possible to make a new approach to the understanding of the nature of chemical compounds and also to use the methods of physicochemical analysis in the development of alloy chemistry, the chemistry of salts, and other important branches of chemistry of enormous significance for practice in the widest sense of the word. As will be seen here also, the progress of modern science traces its roots back to the truly classical investigations of D. I. Mendeleev.

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Mendeleev was not a theoretical scientist, a stranger to the direct development of industrial processes, as, for example, were A. M. Butlerov, Willard Gibbs, and Albert Einstein; in his person we find a harmonious combination of the scientist-innovator whose discoveries meant the beginning of a new era in the development of all chemical thought and of a greater worker in industry and agriculture. Mendeleev constantly regarded his activities as service to his country and people, and he never separated them from his participation in the development of the culture of all mankind. Although materialistic by nature in his creative work and although applying the dialectical method of investigation, D. I. Mendeleev was not sufficiently consistent in his philosophical convictions. This dichotomy was present also in his economic, social and political views. Hence, although Mendeleev did a great deal in his fight for higher culture and the development of the industrial strength of his country, he regarded capitalism as the main force in the fight for the independence of Russia both in the field of industry and agriculture and in the field of science and education. Nevertheless, much that he did was later found to constitute very important contributions to the progress of industry—still more important than he himself could have foreseen on the basis of his views.

We must first consider one of the most important industrial problems, the problem of fuel. Having suggested a formula for calculating the calorific value of a fuel from its chemical composition, Mendeleev went further and went deeply into the analysis and solution of industrial and economic problems associated with the getting of coal. In his treatise "The Future Power that Rests in the Banks of the Donets" (1880) Mendeleev, on the basis of technical and economic data, displayed the problem of developing the Donbass in its full magnitude, and at the same time discussed the future problems of utilizing the coals of Kuznetsk, Kuban, Altai, and the Enisei and Yakutsk regions—problems which could be dealt with only after the Great October Socialist Revolution. It was he who drew the attention of coal chemists to the problem of underground gasification of coal and to the utilization of ammonia in gas works for the manufacture of mineral fertilizers, which has now been effected in our socialist industry.

Being such an ardent innovator and propagandist for the growth of industry, Mendeleev also worked on metallurgy, which is so closely connected with the chemistry of coal. His book "The Iron Industry of the Urals" was written when Mendeleev was sixty five after a long trying personal acquaintance with manufacture in the Urals. Mendeleev suggested the use of the magnetic method of prospecting for iron ores and the method of direct reduction (without blast furnace) of iron from its ores— methods which only now are beginning to be adopted in practice. He insisted on the necessity of utilizing low-grade iron ores and also chromium-manganese ores.

Mendeleev devoted a great deal of attention to the problem of prospecting for oil, getting it, and treating it. In order to study the subject he visited first Baku and then Pennsylvania; he finally worked at the Ragozin oil distillery near Nizhny Novgorod (now Gorky). Mendeleev advanced his theory (the "carbide theory") of the origin of petroleum, made proposals concerning the chemical treatment of petroleum, constructed apparatus for the continuous distillation of petroleum, and suggested the construction of a pipeline from the Caspian to the Black Sea and the use of tankers for the transportation of oil by sea. In his book "A Rational Tariff" Mendeleev raised, for the first time, various questions concerning the development of the chemical industry and the use of new forms of raw material in this industry; his suggestions were implemented in the first three five-year plans for the development of the national economy of the USSR.

Having come forward as a propagandist for the extensive use of mineral fertilizers in agriculture, Mendeleev acquired a piece of land in Boblovo and personally studied the use of mineral fertilizers in practice; what is more, his experiments became so widely known that excursions of students and professors of the Petrov-Razumov Agricultural Academy began to come from Moscow. With the support of the Free Economics Society, Mendeleev carried out pioneering work on potash fertilizers, petitioned for the organization of mining of our native phosphorites, etc. Only much later, at the initiative of Comrade S. M. Kirov, were we able to utilize the Khibin apatites. The "chemicalization" of agriculture is now an established fact which plays an enormous part in raising the productive power and the well-being of our country. Here we must remember with gratitude the name of Mendeleev, raising his voice in defense of progress and pointing out the true road toward the chemicalization of agrotechnics. This happened also in a whole series of branches of industry and agriculture, which, in Mendeleev's figurative expression, utilize science "for prediction and as a tool."

\* \* \*

In the half-century that has passed since the death of the great D. I. Mendeleev his ideas have received further development and consolidation. For long years they have remained as a torch of science, guiding human culture in its victorious advance toward the summits of knowledge and the subjection of nature to the might of man.

A. F. Kapustinsky



Valentin Alekseevich Kargin

Dear Valentin Alekseevich Kargin:

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences congratulate you on the occasion of your fiftieth birthday.

Your varied scientific activity in fields of the colloidal and physical chemistry of macromolecular compounds is valued highly by the scientists of our country.

Kindly accept the very best wishes for your health and further progress in your creative scientific work for the benefit of our Fatherland.

Division of Chemical Sciences of the Academy  
of Sciences of the USSR

and

Editorial Board of the Bulletin of the Academy  
of Sciences of the USSR, Division of Chemical  
Sciences

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# INORGANIC AND ANALYTICAL CHEMISTRY

## SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

### COMMUNICATION 13. PROPERTIES OF PEROXY COMPOUNDS OF ZINC

S. Z. Makarov and L. V. Ladeinova

Study of the system  $\text{Zn}(\text{OH})_2\text{-H}_2\text{O}_2\text{-H}_2\text{O}$  by the solubility method over the temperature range from  $-20^\circ$  to  $+30^\circ$  revealed the presence of the following solid phases:  $\text{ZnO}_2\cdot 2\text{H}_2\text{O}$ ;  $\text{ZnO}_2\cdot 1.5\text{H}_2\text{O}$ ;  $\text{ZnO}_2\cdot \text{H}_2\text{O}$ ;  $\text{ZnO}_2\cdot 0.5\text{H}_2\text{O}$ ,  $\text{ZnO}_2$ ;  $\text{ZnO}_2\cdot 0.5\text{H}_2\text{O}_2\cdot \text{H}_2\text{O}$ ;  $\text{ZnO}_2\cdot \text{H}_2\text{O}_2$  and  $\text{ZnO}_2\cdot 2\text{H}_2\text{O}_2$ . However, apart from  $\text{ZnO}_2\cdot 0.5\text{H}_2\text{O}$ , we were unable to isolate the solid phases in the pure state owing to their interaction with hydrogen peroxide in the residue. In order to study the properties of the peroxy compounds of zinc formed, we prepared the so-called "residues," corresponding to the solid phases of the system admixed with a little equilibrium liquid phase. The conditions for preparing the residues were determined from the solubility curves of the system [1]. Data on the temperature and concentration limits for the existence of the solid phases are given in Table 1.

TABLE 1

Solid phase	Temperature in $^\circ\text{C}$	Limits of $\text{H}_2\text{O}_2$ concentration
$\text{ZnO}_2\cdot 2\text{H}_2\text{O}$	30	3.0—5.0
$\text{ZnO}_2\cdot 1.5\text{H}_2\text{O}$	30	17.0—18.0
$\text{ZnO}_2\cdot \text{H}_2\text{O}$	20	22.0—23.0
$\text{ZnO}_2\cdot 0.5\text{H}_2\text{O}$	-10	22.0—23.0
$\text{ZnO}_2$	0	43.0—44.0
$\text{ZnO}_2\cdot 0.5\text{H}_2\text{O}_2\cdot \text{H}_2\text{O}$	-10	41.0—42.0
$\text{ZnO}_2\cdot \text{H}_2\text{O}_2$	-20	72.0—73.0

In order to avoid the formation of finely crystalline and viscous residues, low  $\text{H}_2\text{O}_2$  concentrations and somewhat high temperatures were used. The residues corresponding to the various solid phases were investigated by thermal and x-ray analysis for tendency to undergo dehydration.

### EXPERIMENTAL

1. Dehydration of Residues. The residues were well pressed off and dried 1) in a desiccator over concentrated sulfuric acid under room conditions; 2) in a drying cupboard at  $60^\circ$ ; 3) in a vacuum drying cupboard at  $50^\circ$ .

The composition of the product during drying over concentrated sulfuric acid was checked by active-oxygen determinations. All residues lost up to 12% of active oxygen during drying, as indicated in Fig. 1. The

TABLE 2

Temperature of heating ( $^\circ\text{C}$ )	Composition (%)			Temperature of heating ( $^\circ\text{C}$ )	Composition (%)		
	ZnO	active oxygen	$\text{H}_2\text{O}$		ZnO	active oxygen	$\text{H}_2\text{O}$
Residue corresponding to $\text{ZnO}_2\cdot 1.5\text{H}_2\text{O}$				Residue corresponding to $\text{ZnO}_2\cdot 0.5\text{H}_2\text{O}$			
70	78.97	12.34	8.69	70	78.17	12.78	9.05
115	80.34	11.78	7.88	115	79.93	11.84	8.23
220	95.88	0.00	4.12	220	97.97	0.00	2.03
400	98.50	0.00	1.50	400	99.56	0.00	0.44
600	99.70	0.00	0.30	600	99.40	0.00	0.60

changes in the compositions of the residues dried in a cupboard at 60° were followed by determinations of active oxygen and water. For the first three hours there was a fall in the contents of active oxygen and water in all residues, but the composition then ceased to change (Fig. 2) and approximated a final composition of  $\text{ZnO}_2 \cdot 0.5 \text{H}_2\text{O}$ . Rapid vacuum drying of the products at 35-40° (Fig. 3) resulted in partial dehydration during the first three hours and increase of the active-oxygen content to about 19.5%. For all residues, the final products of drying had compositions that again approximated

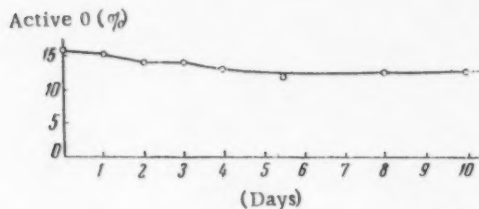


Fig. 1

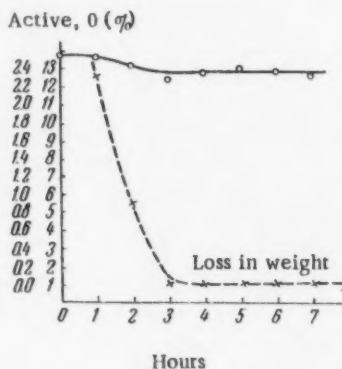


Fig. 2

$\text{ZnO}_2 \cdot 0.5 \text{H}_2\text{O}$ , and not anhydrous zinc peroxide. The triangular diagram (Fig. 4) shows the compositions of residues corresponding to  $\text{ZnO}_2 \cdot 1.5 \text{H}_2\text{O}$  (—●—) and  $\text{ZnO}_2 \cdot 0.5 \text{H}_2\text{O}$  (—○—) and the compositions of these substances during drying (Table 2).

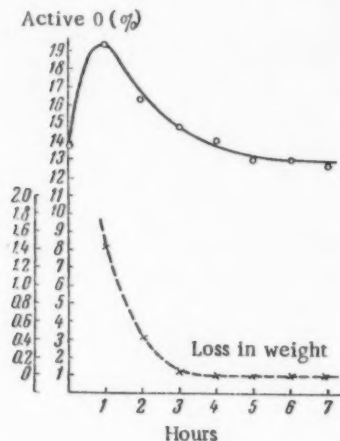


Fig. 3

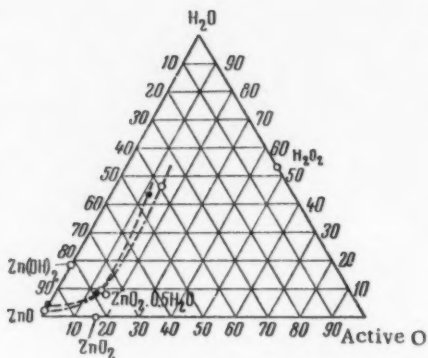


Fig. 4

The form of the curves uniting figurative points indicates that, in the process of drying, residues follow a path from hydrate forms of peroxy compounds of zinc to hydrate forms of zinc oxide without passing through anhydrous zinc peroxide.

**2. Thermal Analysis of the Residues and the Final Products of Drying.** This was carried out by the method of determining heating curves with a pyrometer of the Kurnakov system. The heating curves of  $\text{Zn}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  (Fig. 5) and  $\text{ZnO}$  (Fig. 6) were first determined. The endothermic effect on heating curves of  $\text{Zn}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  at 125° corresponds to the removal of adsorbed water from the hydroxide. Above 125° there remains  $\text{Zn}(\text{OH})_2$ , which decomposes to  $\text{ZnO}$  at 175°. The temperatures are in accord with data in the literature [2].

The exothermic effect at 320° corresponds to the loss of traces of water from the hydroxide and formation of active zinc oxide, which passes into the stable form at about 600°. The same exothermic effect is observed

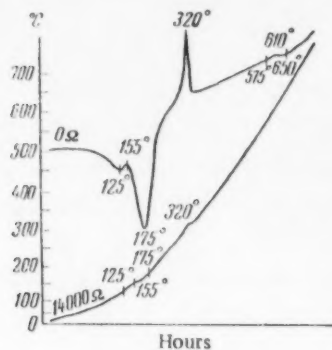


Fig. 5.

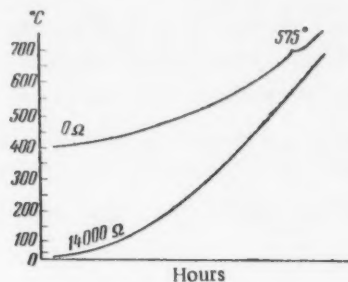


Fig. 6.

also on the differential heating curve of zinc oxide (Fig. 6). This explanation of the effects is in accord with the results of other authors [3-5].

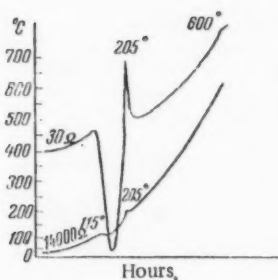


Fig. 7.

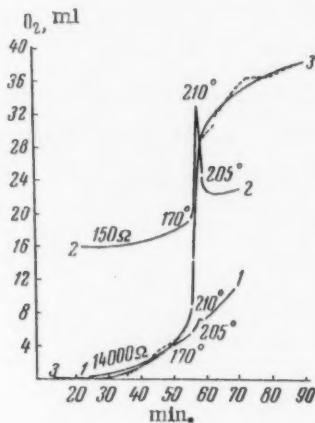


Fig. 8.

The heating curves of residues corresponding to various hydrate forms of zinc peroxide have the form shown in Fig. 7. The endothermic effect at 115° corresponds to the elimination of adsorbed water, and the exothermic effect at 205° corresponds to the elimination of active oxygen and water, and is accompanied by the ejection of the substance from the vessel. The small exothermic effect at 600° corresponds to the transition of active zinc oxide into the more stable form. The residue, corresponding to  $\text{ZnO}_2 \cdot 2\text{H}_2\text{O}$  was dried in a vacuum drying cupboard at 60° until it attained a composition close to  $\text{ZnO}_2 \cdot 0.5\text{H}_2\text{O}$  (77.61%  $\text{ZnO}$ , 11.52% of active oxygen, and 10.8%  $\text{H}_2\text{O}$ ). The heating curve and the amount of gas liberated during heating were determined simultaneously for this product (Fig. 8) (1— straight record; 2— differential record; 3— curve for liberation of oxygen).

There was no endothermic effect, but the exothermic effect at 210°, which was accompanied by a slight explosion, corresponds to the simultaneous elimination of active oxygen and water. Vigorous evolution of gas occurred at the temperature of the exothermic effect.

3. X-Ray Analysis. The residues and the final products of drying were examined in polycrystal cameras with nickel-filtered  $\text{CuK}\alpha$  radiation in a URS-7 apparatus. The x-ray results are in good agreement with the results of Reinhardt [6].

#### SUMMARY

1. The solid phases found in the investigation of the system  $\text{Zn}(\text{OH})_2\text{--H}_2\text{O}_2\text{--H}_2\text{O}$  are stable only when in equilibrium with the corresponding liquid phases. Only  $\text{ZnO}_2 \cdot 0.5\text{H}_2\text{O}$  was isolated as a chemical individual.
2. The final product of the dehydration of the various solid phases of the system is  $\text{ZnO}_2 \cdot 0.5\text{H}_2\text{O}$ .
3. Further prolonged drying of  $\text{ZnO}_2 \cdot 0.5\text{H}_2\text{O}$  at  $110^\circ$  does not give anhydrous zinc peroxide,  $\text{ZnO}_2$ , but is accompanied by decomposition of the peroxide.
4. Thermal analysis showed that  $\text{ZnO}_2 \cdot 0.5\text{H}_2\text{O}$  decomposes with elimination of  $\text{H}_2\text{O}$  and active oxygen at  $180\text{--}190^\circ$ .

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## PHYSICAL CHEMISTRY

### MECHANISM OF THE DISSOCIATION OF A DIATOMIC MOLECULE ON ADSORPTION ON THE SURFACE OF A SEMICONDUCTOR

F. F. Volkenshtein

It may be regarded as experimentally established that in a number of cases a molecule undergoes dissociation when adsorbed. However, there has been no theoretical investigation of this phenomenon. In the present paper we consider the mechanism of such dissociation occurring in the actual adsorption act for the case of a diatomic molecule adsorbed on the surface of an ionic crystal. The part played in this by the free electrons of the lattice is investigated. Our present task consists not in the quantitative evaluation of various quantities, but in the elucidation of the physical mechanism of the phenomenon. It must be pointed out that the mechanism considered here, though a possible mechanism, must not be regarded as the only possible mechanism. In particular, mechanisms in which the free electrons of the lattice do not participate are not considered in the present work and are excluded beforehand by the definition of the problem (see below). Hence, adsorption due to the attraction of an electron cloud from the molecule to the lattice (the so-called "weak" bond), which has been investigated in detail for the case of a univalent atom [1, 2] is completely ignored here in its application to a molecule. This investigation shows that the free electron of the lattice is a determining factor in the rupture of a valence bond of the molecule being adsorbed, and in the simultaneous chemisorption of the dissociation products.

#### 1. Definition of Problem

As adsorbent we shall take an ionic crystal of the type MR (in which M denotes a metal and R a metalloid) built up of singly charged ions  $M^+$  and  $R^-$ , which will be treated as point charges. As adsorbate we shall take a diatomic molecule AB built up of the atoms A and B, each of which has a single valence electron. We shall treat our problem as a three-electron problem: two electrons in the molecule AB effecting a linkage between the atoms A and B, together with a free electron in the crystal lattice of the adsorbent. We shall be interested here in the part played by the free electron.

Ionic crystals used as adsorbents have the most varied crystallographic structures. For the purpose of calculation, however, it is necessary to consider a concrete crystallographic model. It is quite in order for us to select the model that is the most convenient for the purpose of calculation. We may be sure that the mechanism found for the simplest (from the point of view of calculation) model of a crystal will be preserved (qualitatively) for any other crystallographic model. We shall suppose that the crystallographic cell of the adsorbent is a body-centered parallelepiped having the sides  $d_1, d_2, d_3$  ( $d_3 < d_2, d_3 < d_1$ ), as shown in Fig. 1. Such a model allows us to reduce our three-dimensional problem to a series of independent one- and two-dimensional problems. Let the surface  $x = 0$  serve as the adsorbing surface. The half-space  $x < 0$  is the gas phase, and the half-space  $x > 0$  is occupied by a crystal of the adsorbent. Let  $g$  be the number of the metal ion in the lattice; the vector  $g$  has integral components  $g_1, g_2, g_3$ :

$$g = (g_1, g_2, g_3),$$

where

$$\begin{cases} g_1 = 0, 1, 2, 3, \dots \\ g_2, g_3 = 0, \pm 1, \pm 2, \pm 3, \dots \end{cases}$$

Let the line of the nuclei of the molecule AB be normal to the crystal surface, as represented in Fig. 1.

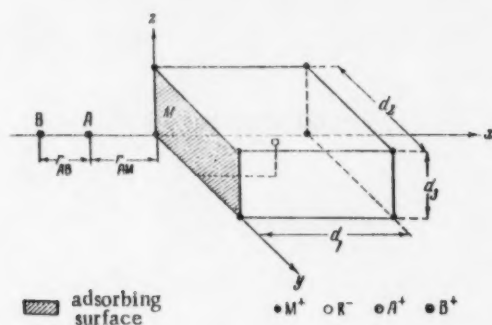


Fig. 1

The distances  $r_{AB}$  and  $r_{AM}$  will enter our problem as parameters. For our three-electron problem the Schrodinger equation will have the form:

$$H\psi = W\psi \quad (1)$$

in which

$$H = \frac{\hbar^2}{2m} (\Delta_1 + \Delta_2 + \Delta_3) + V(x_1) + V(x_2) + V(x_3) + \\ + V(x_1, x_2) + V(x_1, x_3) + V(x_2, x_3) + V_{AB} + V_{AL} + V_{BL}. \quad (2)$$

Here  $x_i$  denotes the set of three spacial coordinates for the  $i$ th electron ( $i = 1, 2, 3$ );  $V(x_i)$  is the potential of the  $i$ th electron in the field of all the ions of the system (i.e., in the field created by the ions  $A^+$  and  $B^+$  and all the  $M^+$  and  $R^-$  ions of the lattice);  $V(x_i x_k)$  is the interaction potential of the  $i$ th and  $k$ th electrons;  $V_{AL}$  and  $V_{BL}$  are the potentials of the ions  $A^+$  and  $B^+$ , respectively, in the field of the lattice;  $V_{AB}$  is the interaction potential of the ions  $A^+$  and  $B^+$ .

The solution of Equation 1 will be sought in the form:

$$\Psi = \sum_{\sigma} \sum_{g} c_{\sigma g} \Phi_{\sigma g}, \quad (3)$$

in which

$$\Phi_{\sigma g} = \frac{1}{V^6} \sum_P \epsilon_P P \{ \omega_{\sigma_1}(s_1) \varphi_A(x_1) \cdot \omega_{\sigma_2}(s_2) \varphi_B(x_2) \cdot \omega_{\sigma_3}(s_3) \varphi_g(x_3) \}. \quad (4)$$

Here  $s_i$  is the spin coordinate of the  $i$ th electron;  $P$  is the electron-transposition operator; the symbol  $\epsilon_P$  has the usual meaning:

$$\varepsilon_P = \begin{cases} = +1 \dots & \text{if } P \text{ is even} \\ = -1 \dots & \text{if } P \text{ is odd} \end{cases}$$

The functions  $\varphi_A$ ,  $\varphi_B$ ,  $\varphi_g$  are spatial atomic functions (we shall regard them as  $\underline{s}$  functions) satisfying the equations

$$\left. \begin{aligned} H_A \varphi_A &= E_A \varphi_A \dots, \text{where } H_A = -\frac{\hbar^2}{2m} \Delta + V_A(x) \\ H_B \varphi_B &= E_B \varphi_B \dots, \text{where } H_B = -\frac{\hbar^2}{2m} \Delta + V_B(x) \\ H_g \varphi_g &= E_g \varphi_g \dots, \text{where } H_g = -\frac{\hbar^2}{2m} \Delta + V_g(x) \end{aligned} \right\} \quad (5)$$

Here  $V_A(x)$ ,  $V_B(x)$ ,  $V_g(x)$  are potentials of electrons in the fields of the  $A^+$  ion, of the  $B^+$  ion, and of the  $g$ th metal ion of the lattice ( $M^+$ ), respectively. The function  $\omega_{\sigma_i}$  is a spin wave function corresponding to the spin quantum number  $\sigma_i$ , which can have two values:

$$\sigma_i = \begin{cases} = +\frac{1}{2} = p \dots & (\text{positive spin}) \\ = -\frac{1}{2} = n \dots & (\text{negative spin}) \end{cases} \quad (6)$$

The numbers  $\sigma_1, \sigma_2, \sigma_3$  can be regarded as components of the vector  $\sigma$ :

$$\sigma = (\sigma_1, \sigma_2, \sigma_3).$$

In accordance with (6), the vector  $\sigma$  can clearly have the following eight values:

$$= (ppp), (ppn), (pnp), (npp), (nnp), (npn), (pnn), (nnn).$$

The summation in (3) is to be carried over all the values of  $\sigma_1, \sigma_2, \sigma_3, g_1, g_2, g_3$ .

The problem amounts to the determination of the coefficients  $c_{\sigma g}$  in (3); they are determined from the system of equations:

$$\frac{\partial I}{\partial c_{\sigma g}} = \sum_{\sigma'} \sum_{g'} c_{\sigma' g'} (H_{\sigma' g'}^{\sigma g} - W S_{\sigma' g'}^{\sigma g}) = 0, \quad (7)$$

in which

$$I = \sum_s \int \Psi^* (H - W) \Psi d\tau.$$

In this

$$\begin{cases} H_{\sigma'g'}^{\sigma g} = \sum_s \int \Phi_{\sigma g}^* H \Phi_{\sigma'g'} d\tau \\ S_{\sigma'g'}^{\sigma g} = \sum_s \int \Phi_{\sigma g}^* \Phi_{\sigma'g'} d\tau \end{cases} \quad \begin{matrix} (8) \\ (9) \end{matrix}$$

## 2. Calculation of the Matrix Elements

As can be shown, the matrix elements of (8) have the following properties:

$$H_{\sigma'g'}^{\sigma g} = 0, \dots, \text{ if } \sigma_1 + \sigma_2 + \sigma_3 \neq \sigma'_1 + \sigma'_2 + \sigma'_3 \quad (10a)$$

$$H_{\sigma'g'}^{\sigma g} = H_{\sigma g}^{\sigma'g'} \quad (10b)$$

$$H_{\sigma'g'}^{\sigma g} = H_{-\sigma'g'}^{-\sigma g} \quad (10c)$$

In the further treatment we shall make use of these properties.

Let us consider the calculation of the matrix elements of (8). We will introduce the symbols:

$$\left. \begin{aligned} S_{l'}^l &= \int \varphi_l(x_i) \varphi_{l'}(x_i) d\tau_i \\ Q_{l'}^l &= \int \varphi_l(x_i) \{V(x_i) - V_{l'}(x_i)\} \varphi_{l'}(x_i) d\tau_i \\ R_{l'm'}^{lm} &= \int \varphi_l(x_i) \varphi_m(x_k) V(x_i, x_k) \varphi_{l'}(x_i) \varphi_{m'}(x_k) d\tau_i d\tau_k \end{aligned} \right\} \quad (11)$$

In which  $\underline{l}, k = 1, 2, 3, \underline{l}$  not being equal to  $\underline{k}$ ;  $\underline{l}, \underline{m}, \underline{l}', \underline{m}'$  may have the values:

$$\left. \begin{aligned} l, m &= A, B, g \\ l', m' &= A, B, g' \end{aligned} \right\}$$

Let us make the following approximations:

a) We shall consider that the disturbance due to the break in the lattice is felt only by the first (surface) layer of atoms [atoms having the numbers  $\underline{g} = (0, g_2, g_3)$ ].

b) We shall consider that the disturbing effect of the foreign molecule AB is felt only by the nearest atom of the lattice [the atom  $\underline{g} = (0, 0, 0)$ ].

c) We shall consider that the wave functions  $\varphi_{\underline{g}}$  of two adjacent atoms of the lattice overlap only to a slight extent.

We may then assume:

$$S_{l'}^l = \begin{cases} = 1, \dots, & \text{if } l = l' \text{ (for any value of } l) \\ = S_{AB} \dots, & \text{if } l = A, l' = B \text{ or } l = B, l' = A \\ = S_{AM} \dots, & \text{if } l = A, l' = M \text{ or } l = M, l' = A \\ = S_{BM} \dots, & \text{if } l = B, l' = M \text{ or } l = M, l' = B \\ = 0 \dots\dots & \text{in all other cases} \end{cases} \quad (12a)$$

$$Q_{l,l'}^l = \left\{ \begin{array}{ll} = \alpha_A \dots, & \text{if } l = l' = A \\ = \alpha_B \dots, & \text{if } l = l' = B \\ = \alpha_M \dots, & \text{if } l = l' = M \\ = \alpha \dots, & \text{if } l = l' = \mathbf{g} \neq (0, g_2, g_3) \\ = \alpha' \dots, & \text{if } l = l' = \mathbf{g} = (0, g_2, g_3) \neq (0, 0, 0) \\ = \beta_{AB} \dots, & \text{if } l = A, l' = B \\ = \beta_{BA} \dots, & \text{if } l = B, l' = A \\ = \beta_{AM} \dots, & \text{if } l = A, l' = M \\ = \beta_{MA} \dots, & \text{if } l = M, l' = A \\ = \beta_{BM} \dots, & \text{if } l = B, l' = M \\ = \beta_{MB} \dots, & \text{if } l = M, l' = B \\ = \beta \dots, & \text{if } l = \mathbf{g} = (g_1, g_2, g_3) \neq (0, g_2, g_3), \\ & l' = \mathbf{g}' = (g_1, g_2, g_3 \pm 1) \\ = \beta \dots, & \text{if } l = \mathbf{g} = (0, g_2, g_3), l' = \mathbf{g}' = (0, g_2, g_3 \pm 1) \\ = 0 \dots, & \text{in all other cases} \end{array} \right\} \quad (12b)$$

$$R_{l,m}^{l'm'} = \left\{ \begin{array}{ll} = \eta_{AB} \dots, & \text{if } l = l' = A, m = m' = B \\ = \eta_{AM} \dots, & \text{if } l = l' = A, m = m' = B \\ = \eta_{BM} \dots, & \text{if } l = l' = B, m = m' = M \\ = \zeta_{AB} \dots, & \text{if } l = m' = A, l' = m = B \\ = \zeta_{AM} \dots, & \text{if } l = m' = A, l' = m = M \\ = \zeta_{BM} \dots, & \text{if } l = m' = B, l' = m = M \\ = 0 \dots & \text{in all other cases} \end{array} \right\} \quad (12c)$$

in which the symbol **M** denotes an atom of the lattice of number  $\mathbf{g} = (0, 0, 0)$ .

In calculating the matrix elements of (8), we shall introduce the approximations (12a, b, and c) and neglect terms containing squares and higher powers of nonorthogonal integrals  $S_l^l$  (in which  $l$  is not equal to  $l'$ ). With these approximations, all the matrix elements of (8) for which

$$\mathbf{g}' - \mathbf{g} \neq (0, 0, 0), (0, 0, \pm 1)$$

are reduced to zero.

Let us write:

$$\left\{ \begin{array}{l} \varepsilon = E_A + E_B + E_M + V_{AB} + V_{AL} + V_{BL} \\ C = \alpha_A + \alpha_B + \alpha_M + \eta_{AB} + \eta_{AM} + \eta_{BM} \\ C_{AB} = \alpha_A + \alpha_B + \eta_{AB} \\ C_{AM} = \alpha_A + \alpha_M + \eta_{AM} \\ C_{BM} = \alpha_B + \alpha_M + \eta_{BM} \\ A_{AB} = (\beta_{AB} + \beta_{BA}) S_{AB} + \zeta_{AB} \\ A_{AM} = (\beta_{AM} + \beta_{MA}) S_{AM} + \zeta_{AM} \\ A_{BM} = (\beta_{BM} + \beta_{MB}) S_{BM} + \zeta_{BM} \end{array} \right\} \quad (13)$$

It can be shown that, in accordance with (10b and c) and (12a, b, and c), we obtain the following for the matrix elements of (8) in which we are interested:

For diagonal elements ( $\sigma = \sigma'$ ):

$$\begin{aligned}
 H_{pppg'}^{pppg} = H_{nnng'}^{nnng} &= \left\{ \begin{aligned} &= \varepsilon + C - A_{AB} - A_{AM} - A_{BM} \dots, \text{ if } g' = g = (0, 0, 0) \\ &= \varepsilon + \alpha' + C_{AB} - A_{AB} \dots, \text{ if } g' = g = \\ &\quad = (0, g_2, g_3) \neq (0, 0, 0) \\ &= \varepsilon + \alpha + C_{AB} - A_{AB} \dots, \text{ if } g' = g \neq (0, g_2, g_3) \\ &= \beta' \dots, \text{ if } g' = (0, g_2, g_3 \pm 1), g = (0, g_2, g_3) \\ &= \beta \dots, \text{ if } g' = (g_1, g_2, g_3 \pm 1), g \neq (0, g_2, g_3) \\ &= 0 \dots \text{ in all other cases} \end{aligned} \right\} \\
 H_{ppng'}^{ppng} = H_{nnpg'}^{nnpg} &= \left\{ \begin{aligned} &= \varepsilon + C - A_{AB} \dots, \text{ if } g' = g = (0, 0, 0) \\ &= \varepsilon + \alpha' + C_{AB} - A_{AB}, \text{ if } g' = g = \\ &\quad = (0, g_2, g_3) \neq (0, 0, 0) \\ &= \varepsilon + \alpha + C_{AB} - A_{AB}, \text{ if } g' = g \neq (0, g_2, g_3) \\ &= \beta' \dots, \text{ if } g' = (0, g_2, g_3 \pm 1), g = (0, g_2, g_3) \\ &= \beta \dots, \text{ if } g' = (g_1, g_2, g_3 \pm 1), g \neq (0, g_2, g_3) \\ &= 0 \dots \text{ in all other cases} \end{aligned} \right\} \quad (14a) \\
 H_{pnpg'}^{pnpg} = H_{npgg'}^{npgg} &= \left\{ \begin{aligned} &= \varepsilon + C - A_{AM} \dots, \text{ if } g' = g = (0, 0, 0) \\ &= \varepsilon + \alpha' + C_{AB} \dots, \text{ if } g' = g = \\ &\quad = (0, g_2, g_3) \neq (0, 0, 0) \\ &= \varepsilon + \alpha + C_{AB} \dots, \text{ if } g' = g \neq (0, g_2, g_3) \\ &= \beta' \dots, \text{ if } g' = (0, g_2, g_3 \pm 1), g = (0, g_2, g_3) \\ &= \beta \dots, \text{ if } g' = (g_1, g_2, g_3 \pm 1), g \neq (0, g_2, g_3) \\ &= 0 \dots \text{ in all other cases} \end{aligned} \right\} \\
 H_{nppg'}^{nppg} = H_{pnng'}^{pnng} &= \left\{ \begin{aligned} &= \varepsilon + C - A_{BM} \dots, \text{ if } g' = g = (0, 0, 0) \\ &= \varepsilon + \alpha' + C_{AB} \dots, \text{ if } g' = g = \\ &\quad = (0, g_2, g_3) \neq (0, 0, 0) \\ &= \varepsilon + \alpha + C_{AB} \dots, \text{ if } g' = g \neq (0, g_2, g_3) \\ &= \beta' \dots, \text{ if } g' = (0, g_2, g_3 \pm 1), g = (0, g_2, g_3) \\ &= \beta \dots, \text{ if } g' = (g_1, g_2, g_3 \pm 1), g \neq (0, g_2, g_3) \\ &= 0 \dots \text{ in all other cases} \end{aligned} \right\}
 \end{aligned}$$

For nondiagonal elements ( $\sigma \neq \sigma'$ ):

$$\begin{aligned}
 H_{pnpg'}^{pnpg} = H_{nnpg'}^{nnpg} = H_{nppg'}^{nppg} = H_{pnng'}^{pnng} &= \left\{ \begin{aligned} &= -A_{AB} \dots, \text{ if } g' = g \\ &= 0 \dots \text{ in all other cases} \end{aligned} \right\} \\
 H_{ppng'}^{ppng} = H_{nnpg'}^{nnpg} = H_{pppg'}^{pppg} = H_{nnpg'}^{nnpg} &= \left\{ \begin{aligned} &= -A_{AM} \dots, \text{ if } g' = g = \\ &\quad = (0, 0, 0) \\ &= 0 \dots \text{ in all other cases} \end{aligned} \right\} \quad (14b) \\
 H_{ppng'}^{ppng} = H_{nnpg'}^{nnpg} = H_{pppg'}^{pppg} = H_{nnpg'}^{nnpg} &= \left\{ \begin{aligned} &= -A_{BM} \dots, \text{ if } g' = g = \\ &\quad = (0, 0, 0) \\ &= 0 \dots \text{ in all other cases} \end{aligned} \right\}
 \end{aligned}$$



In accordance with (10a) all the remaining matrix elements of (8) are reduced to zero.

Let us now turn to the matrix elements of (9). If in the calculation of these matrix elements we neglect terms containing squares (or higher powers) of nonorthogonal integrals  $S_{\mathbf{l}}^2$ , (in which  $\mathbf{l}$  is not equal to  $\mathbf{l}'$ ), it can be shown that we obtain:

$$S_{\sigma' \mathbf{g}'}^{\sigma \mathbf{g}} = \begin{cases} = 1, \dots, & \text{if } \sigma = \sigma' \quad \mathbf{g} = \mathbf{g}' \\ = 0, \dots & \text{in all other cases} \end{cases} \quad (15)$$

### 3. Basic System of Equations

We return now to Equations (7). According to (10a), in the summation with respect to  $\sigma'$  in (7), only those terms are retained for which  $\sigma'$  differs from  $\sigma$  by the transposition of two unlike spins. The system of equations (7) breaks down into four independent systems corresponding to the four possible values of the resultant spin:

$$\sigma_1 + \sigma_2 + \sigma_3 = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}.$$

We have:

$$\left\{ \begin{aligned} c_{pppg}W &= \sum_{\mathbf{g}'} c_{pppg'} H_{pppg'}^{pppg} \end{aligned} \right. \quad (16a)$$

$$\left\{ \begin{aligned} c_{ppng}W &= \sum_{\mathbf{g}'} \{ c_{ppng'} H_{ppng'}^{ppng} + c_{pnpg'} H_{pnpg'}^{ppng} + c_{nppg'} H_{nppg'}^{ppng} \} \\ c_{pnpg}W &= \sum_{\mathbf{g}'} \{ c_{ppng'} H_{ppng'}^{pnpg} + c_{pnpg'} H_{pnpg'}^{pnpg} + c_{nppg'} H_{nppg'}^{pnpg} \} \end{aligned} \right. \quad (16b)$$

$$\left\{ \begin{aligned} c_{nppg}W &= \sum_{\mathbf{g}'} \{ c_{ppng'} H_{ppng'}^{nppg} + c_{pnpg'} H_{pnpg'}^{nppg} + c_{nppg'} H_{nppg'}^{nppg} \} \end{aligned} \right. \quad (16c)$$

$$\left\{ \begin{aligned} c_{nnpg}W &= \sum_{\mathbf{g}'} \{ c_{nnpg'} H_{nnpg'}^{nnpg} + c_{nnpng'} H_{nnpng'}^{nnpg} + c_{pnng'} H_{pnng'}^{nnpg} \} \\ c_{nnpng}W &= \sum_{\mathbf{g}'} \{ c_{nnpg'} H_{nnpg'}^{nnpng} + c_{nnpng'} H_{nnpng'}^{nnpng} + c_{pnng'} H_{pnng'}^{nnpng} \} \\ c_{pnng}W &= \sum_{\mathbf{g}'} \{ c_{nnpg'} H_{nnpg'}^{pnng} + c_{nnpng'} H_{nnpng'}^{pnng} + c_{pnng'} H_{pnng'}^{pnng} \} \\ c_{nnng}W &= \sum_{\mathbf{g}'} c_{nnng'} H_{nnng'}^{nnng} \end{aligned} \right. \quad (16d)$$

Here, in the summation with respect to  $\mathbf{g}$ , only three terms are retained:

$$\mathbf{g}' = (\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3), (\mathbf{g}_1, \mathbf{g}_3, \mathbf{g}_2 - 1), (\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3 + 1).$$

From a comparison of Equation (16a) with Equation (16d) and also of Equation (16d) with Equation (16b) we obtain from Equation (10c).

$$c_{-\sigma, \mathbf{g}} = C c_{\sigma, \mathbf{g}} \quad (17)$$

in which  $C$  is an arbitrary factor. Let us suppose that

$$C = 0 \quad (18)$$

The problem amounts to the solution of Equations (16a) and (16b).

Equations (16a) cannot interest us. In fact, the solution of these equations leads to states of the system that are characterized both by absence of a bond between the atoms A and B and also by absence of a bond between each of these atoms and the lattice.

Let us suppose that

$$c_{pppg} = 0 \quad (19)$$

and turn to the solution of Equation (16b). We will rewrite these equations, introducing new unknowns in place of the unknowns  $c_{ppng}$ ,  $c_{pnpg}$ ,  $c_{nppg}$ :

$$\left. \begin{aligned} x_g = x(g_1, g_2, g_3) &= \frac{1}{2} (c_{pnpg} - c_{nppg}) \\ y_g = y(g_1, g_2, g_3) &= \frac{1}{3} \left( c_{ppng} - \frac{1}{2} c_{pnpg} - \frac{1}{2} c_{nppg} \right) \\ z_g = z(g_1, g_2, g_3) &= \frac{1}{3} (c_{ppng} + c_{pnpg} + c_{nppg}) \end{aligned} \right\} \quad (20)$$

and substituting the Expressions (14a and b) for the matrix elements  $H_{\sigma g}^{\sigma g}$  in (16b). After simple transformations, the Equation (16b) then takes the form:

For  $g \neq (0, g_2, g_3)$ :

$$\left. \begin{aligned} x(g_1, g_2, g_3) (\varepsilon - W + \alpha + C_{AB} + A_{AB}) + \\ + [x(g_1, g_2, g_3 - 1) + x(g_1, g_2, g_3 + 1)] \beta = 0 \\ y(g_1, g_2, g_3) (\varepsilon - W + \alpha + C_{AB} - A_{AB}) + \\ + [y(g_1, g_2, g_3 - 1) + y(g_1, g_2, g_3 + 1)] \beta = 0 \\ z(g_1, g_2, g_3) (\varepsilon - W + \alpha + C_{AB} - A_{AB}) + \\ + [z(g_1, g_2, g_3 - 1) + z(g_1, g_2, g_3 + 1)] \beta = 0 \end{aligned} \right\} \quad (21)$$

For  $g = (0, g_2, g_3) \neq (0, 0, g_3)$ :

$$\left. \begin{aligned} x(0, g_2, g_3) (\varepsilon - W + \alpha' + C_{AB} + A_{AB}) + \\ + [x(0, g_2, g_3 - 1) + x(0, g_2, g_3 + 1)] \beta' = 0 \\ y(0, g_2, g_3) (\varepsilon - W + \alpha' + C_{AB} - A_{AB}) + \\ + [y(0, g_2, g_3 - 1) + y(0, g_2, g_3 + 1)] \beta' = 0 \\ z(0, g_2, g_3) (\varepsilon - W + \alpha' + C_{AB} - A_{AB}) + \\ + [z(0, g_2, g_3 - 1) + z(0, g_2, g_3 + 1)] \beta' = 0 \end{aligned} \right\} \quad (22)$$

For  $g = (0, 0, g_3) \neq (0, 0, 0)$ :

$$\left. \begin{aligned}
& x(0, 0, g_3)(\varepsilon - W + \alpha' + C_{AB} + A_{AB}) + \\
& \quad + [x(0, 0, g_3 - 1) + x(0, 0, g_3 + 1)]\beta' = 0 \\
& y(0, 0, g_3)(\varepsilon - W + \alpha' + C_{AB} - A_{AB}) + \\
& \quad + [y(0, 0, g_3 - 1) + y(0, 0, g_3 + 1)]\beta' = 0 \\
& z(0, 0, g_3)(\varepsilon - W + \alpha' + C_{AB} - A_{AB}) + \\
& \quad + [z(0, 0, g_3 - 1) + z(0, 0, g_3 + 1)]\beta' = 0 \\
& \text{for } \mathbf{g} = (0, 0, 0): \\
& x(0, 0, 0)\left(\varepsilon - W + C + A_{AB} - \frac{1}{2}A_{AM} - \frac{1}{2}A_{BM}\right) + \\
& \quad + [x(0, 0, -1) + x(0, 0, +1)]\beta' = \frac{3}{2}y(0, 0, 0)(A_{BM} - A_{AM}) \\
& y(0, 0, 0)\left(\varepsilon - W + C - A_{AB} + \frac{1}{2}A_{AM} + \frac{1}{2}A_{BM}\right) + \\
& \quad + [y(0, 0, -1) + y(0, 0, +1)]\beta' = \frac{1}{2}x(0, 0, 0)(A_{BM} - A_{AM}) \\
& z(0, 0, 0)(\varepsilon - W + C - A_{AB} - A_{AM} - A_{BM}) + \\
& \quad + [z(0, 0, -1) + z(0, 0, +1)]\beta' = 0
\end{aligned} \right\} \quad (23)$$

We obtain three mutually independent systems of equations (21), (22), and (23). This result is a consequence of the crystallographic model we have selected.

Equations (21) and (22) have trivial solutions which cannot interest us. In fact Equations (21) lead to states of the system in which the electron is in the body conductivity zone of the crystal, i.e., remains free. These states do not give adsorption. Equation (22) leads to the states in which the electron is in the surface conductivity zones, and these also do not give adsorption.

We assume that

$$x_{\mathbf{g}} = y_{\mathbf{g}} = z_{\mathbf{g}} = 0 \text{ for all values of } \mathbf{g} \neq (0, 0, g_3) \quad (24)$$

In this case, in accordance with (18), (19), (20), and (24), the wave function (3) takes the form:

$$\begin{aligned}
\Psi = \sum_{\mathbf{g}} \{ & x_{\mathbf{g}} + y_{\mathbf{g}} [\Phi_{ppng} - \Phi_{nppg}] + (x_{\mathbf{g}} - y_{\mathbf{g}}) [\Phi_{pnpg} - \Phi_{ppng}] + \\
& + z_{\mathbf{g}} [\Phi_{ppng} + \Phi_{pnpg} + \Phi_{nppg}] \}
\end{aligned} \quad (25)$$

Here  $\mathbf{g} = (0, 0, g_3)$  and the summation is made over all values of  $g_3$  (in the further treatment we shall omit the subscript 3 in  $g_3$ ). The expressions in the first and second pairs of square brackets in (25) represent states expressing the bonds of the atoms A and B, respectively, with the lattice.

The problem amounts to finding the coefficients  $x(0, 0, g)$ ,  $y(0, 0, g)$ ,  $z(0, 0, g)$ , which are determined from Equations (23). These equations may be satisfied by solutions of two types:

I. Solutions of the first type ("periodic" solutions):

$$\left. \begin{aligned}
x(0, 0, g) &= X \sin \lambda g \\
y(0, 0, g) &= Y \sin \mu g \\
z(0, 0, g) &= Z \sin \mu g
\end{aligned} \right\}, \quad (26)$$

in which  $X$ ,  $Y$ , and  $Z$  are arbitrary coefficients and  $\lambda$  and  $\mu$  are real parameters. As can be readily shown, two cases are possible:

$$\begin{aligned} \text{a) } X \neq 0, Y = 0, Z = 0. & \quad (26a) \\ \text{b) } X = 0, Y \neq 0 \text{ where } X = 0, Z \neq 0. & \quad (26b) \end{aligned}$$

As we shall see in the next section, solutions of the type (26) lead to states of the system in which the electron of the lattice remains free (belongs to the surface conductivity zone of the crystal) and takes no part in adsorption.

## II. Solutions of the second type ("dying away" solutions):

$$\left. \begin{aligned} x(0, 0, g) &= X e^{i\lambda|g|} \\ y(0, 0, g) &= Y e^{i\mu|g|} \\ z(0, 0, g) &= Z e^{i\mu|g|} \end{aligned} \right\} \quad (27)$$

in which  $X$ ,  $Y$ , and  $Z$  are unknown coefficients that must be determined, and, in general,  $\lambda$  and  $\mu$  are complex parameters:

$$\left. \begin{aligned} \lambda &= \lambda' + i\lambda'' \\ \mu &= \mu' + i\mu'' \end{aligned} \right\} \quad (28)$$

(here,  $\lambda'$ ,  $\lambda''$ ,  $\mu'$ ,  $\mu''$ , are real parameters). It may be noted that, as the wave function must remain finite to infinity, it must be considered that:

$$\lambda'' \geq 0, \mu'' \geq 0. \quad (29)$$

Here we have two cases:

$$\begin{aligned} \text{a) } X = 0, Y = 0, Z \neq 0 & \quad (27a) \\ \text{b) } X \neq 0, Y \neq 0, Z = 0 & \quad (27b) \end{aligned}$$

As we shall see in the next section, solutions of the type (27) lead to states of the system in which the electron of the lattice is localized on a local level arising in the energy spectrum of the crystal when the molecule AB approaches it.

## 4. The Two Types of Solutions

Let us examine the different solutions of Equations (23).

1a) Substituting (26) and (26a) in Equations (23), we obtain:

$$W = W_\lambda = \varepsilon + \alpha' + (C_{AB} + A_{AB}) + 2\beta' \cos \lambda. \quad (30)$$

As will be seen, the energy of the system is made up of the energy of the free electron in the surface conductivity zone and the energy of the molecule AB in the field of the lattice.

In accordance with (26) and (26a), the wave function (25) takes the form:

$$\Psi = X \sum_g \sin \lambda g (\Phi_{pnpg} - \Phi_{nppg}) \quad (31)$$

in which  $X$  is determined by the standardization conditions and the parameter  $\lambda$  remains arbitrary. The state (31) corresponds to a bond between the atoms  $A$  and  $B$  and absence of a bond between them and the lattice.

Ib) Substituting (26) and (26b) in (23), we obtain:

$$W = W_\mu = \varepsilon + \alpha' + (C_{AB} - A_{AB}) + 2\beta' \cos \mu. \quad (32)$$

In accordance with (26) and (26b), the wave function (25) in this case takes the form:

$$\Psi = C \sum_g \sin \mu g \{(\Phi_{pnpg} + \Phi_{nppg}) + (\Phi_{ppng} + \Phi_{pnpg}) + C'(\Phi_{nppg} + \Phi_{pnpg})\} \quad (33)$$

In which the parameter  $\mu$  remains arbitrary,  $C$  is determined from standardization conditions, and  $C'$  remains arbitrary;  $C = Y + \frac{1}{2} Z$  and  $C' = -(2Y - \frac{1}{2} Z) / (Y + \frac{1}{2} Z)$ . The state (33) corresponds both to absence of a bond between the atoms  $A$  and  $B$  and to absence of bonds between each of them and the lattice.

IIa) We shall not examine here the solution of (27) for the case (27a). It can be shown that this solution leads to a state of the system which, like the state (33), does lead to a bond between the atoms. This state does not result in adsorption and is of no interest to us.

IIb) Let us examine the solution of (27) for the case (27b). In this case Equation (23) may be rewritten as follows ( $g \neq 0$ ):

$$\left. \begin{aligned} X e^{i\lambda|g|} (\varepsilon - W + \alpha' + C_{AB} + A_{AB} + 2\beta' \cos \lambda) &= 0 \\ Y e^{i\mu|g|} (\varepsilon - W + \alpha' + C_{AB} - A_{AB} + 2\beta' \cos \mu) &= 0 \\ X \left( \varepsilon - W + C + A_{AB} - \frac{1}{2} A_{AM} - \frac{1}{2} A_{BM} + 2\beta' e^{i\lambda} \right) &= Y \frac{3}{2} (A_{BM} - A_{AM}) \\ Y \left( \varepsilon - W + C - A_{AB} + \frac{1}{2} A_{AM} + \frac{1}{2} A_{BM} + 2\beta' e^{i\mu} \right) &= X \frac{1}{2} (A_{BM} - A_{AM}) \end{aligned} \right\} \quad (34)$$

The conditions for the compatibility of these equations take the form:

$$W = \varepsilon + \alpha' + (C_{AB} + A_{AB}) + 2\beta' \cos \lambda = \varepsilon + \alpha' + (C_{AB} - A_{AB}) + 2\beta' \cos \mu \quad (35)$$

$$(a + 2i\beta' \sin \lambda)(b + 2i\beta' \sin \mu) = c \quad (36)$$

In which

$$\left. \begin{aligned} a &= \left( C_{AM} - \frac{1}{2} A_{AM} \right) + \left( C_{BM} - \frac{1}{2} A_{BM} \right) - (\alpha_A + \alpha_B + \alpha_M + \alpha') \\ b &= \left( C_{AM} + \frac{1}{2} A_{AM} \right) + \left( C_{BM} + \frac{1}{2} A_{BM} \right) - (\alpha_A + \alpha_B + \alpha_M + \alpha') \\ c &= \frac{3}{4} (A_{AM} - A_{BM})^2 \end{aligned} \right\} \quad (37)$$

It follows from (35) that, in order that  $W$  may have a real value, it must be considered that in (28):

$$\lambda' = l\pi, \mu' = m\pi, \quad (38)$$

in which  $l$  and  $m$  are any integers.

The values of  $\lambda$  and  $\mu$  are fixed by Equations (35) and (36). These equations can be readily solved with respect to  $\lambda$  and  $\mu$  if we assume that:

$$e^{\lambda''} \gg 1, e^{\mu''} \gg 1. \quad (39)$$

In this case Equations (35) and (36) give two solutions  $\lambda_1, \mu_1$  and  $\lambda_2, \mu_2$ :

$$\left. \begin{aligned} 2\beta'(-1)^k \cosh \lambda_k'' &= -(\alpha' + C_{AB} + A_{AB}) + C + \\ &+ (-1)^k \sqrt{A_{AB}^2 + A_{AM}^2 + A_{BM}^2 - A_{AB}A_{AM} - A_{AB}A_{BM} - A_{AM}A_{BM}} \\ 2\beta'(-1)^m \cosh \mu_k'' &= -(\alpha' + C_{AB} - A_{AB}) + C + \\ &+ (-1)^k \sqrt{A_{AB}^2 + A_{AM}^2 + A_{BM}^2 - A_{AB}A_{AM} - A_{AB}A_{BM} - A_{AM}A_{BM}} \end{aligned} \right\} \quad (40)$$

whence, by substitution of (40) in (35):

$$W = W_k = \varepsilon + C + (-1)^k \sqrt{A_{AB}^2 + A_{AM}^2 + A_{BM}^2 - A_{AB}A_{AM} - A_{AB}A_{BM} - A_{AM}A_{BM}}, \quad (41)$$

in which  $k = 1, 2$ . We obtain two local levels  $W_1$  and  $W_2$  ( $W_1 < W_2$ ). It is obvious that  $l_k$  and  $m_k$  in (40) must be regarded as even or odd according as the right-hand side of (40) is positive or negative.

On the basis of (35) and in accordance with (28) and (38), the Conditions (38) may be rewritten ( $\beta'$  being greater than 0) as:

$$\left. \begin{aligned} |W_k - (\varepsilon + \alpha' + C_{AB} + A_{AB})| &= 2\beta' \cosh \lambda'' \gg 2\beta' \\ |W_k - (\varepsilon + \alpha' + C_{AB} - A_{AB})| &= 2\beta' \cosh \mu'' \gg 2\beta' \end{aligned} \right\} \quad (42)$$

in which  $k = 1, 2$ . We see, therefore, that Equation 41 for the local levels  $W_1$  and  $W_2$  is valid on the assumption that these levels are sufficiently far removed from the energy zones (30) and (32), so that the distance between each of these levels and the middles of the zones (30) and (32) is great in comparison to the half-width of a zone.

The wave functions  $\psi_1$  and  $\psi_2$  corresponding to the local levels  $W_1$  and  $W_2$  may, in accordance with (25), (27), and (27b), be written in the following form:

$$\Psi_k = \sum_g \{x_g^k (\Phi_{pnpq} - \Phi_{npqg}) + y_g^k (\Phi_{pqng} - \Phi_{npqg}) + y_g^k (\Phi_{pqng} - \Phi_{pnpq})\}, \quad (43)$$

in which  $k = 1, 2$  and



$$\left. \begin{aligned} x_g^k &= X_k (-1)^{l_k g} e^{-\lambda_k |g|} \\ y_g^k &= Y_k (-1)^{m_k g} e^{-\mu_k |g|} \end{aligned} \right\} \quad (44)$$

Here the values of  $\lambda_k^*$  and  $\mu_k^*$  are given by Equations 40, and  $X_k$  and  $Y_k$  are related as follows (in accordance with Equations 34, 35 and 40):

$$\begin{aligned} \frac{X_k}{Y_k} &= \frac{A_{AB} - \frac{1}{2} A_{AM} - \frac{1}{2} A_{BM}}{\frac{1}{2} (A_{AM} - A_{BM})} + \\ &+ \frac{(-1)^h \sqrt{A_{AB}^2 + A_{AM}^2 + A_{BM}^2 - A_{AB} A_{AM} - A_{AB} A_{BM} - A_{AM} A_{BM}}}{\frac{1}{2} (A_{AM} - A_{BM})}, \end{aligned} \quad (45)$$

In the states represented by (43), both the bond between the atoms A and B and also the bonds formed by each of them with the lattice are included. It will be seen that the wave functions (43) rapidly fade away as  $|g|$  increases, and the greater  $\lambda_k^*$  and  $\mu_k^*$ , the more rapidly this occurs. In other words, the degree of localization of the electron of the lattice in the local level  $W_k$  is the greater, the greater the inequality (42).

Let us examine the limiting case:  $r_{AB} = \infty$ ,  $r_{AM} = \text{const}$  (Fig. 1). In this case, according to (13), (12a, b, c) and (35):

$$C = C_{AM}, A_{AB} = A_{BM} = 0, \lambda = \mu. \quad (46)$$

Substituting (46) in (41), we have ( $A_{AM}$  being less than zero):

$$W = \epsilon + C_{AM} \pm A_{AM}. \quad (47)$$

In accordance with (43), (45), and (40), the wave function for the lower of these levels takes the form:

$$\Psi_1 = 2X_1 \sum_g (-1)^{l_k g} e^{-\lambda_k |g|} (\Phi_{ppng} - \Phi_{nppg}). \quad (48)$$

It will be seen that in this limiting case the link between the lattice and atom B disappears, and only the link between the lattice and atom A is preserved. We obtained a free atom B and an atom A which is attached to the crystal by a strong homopolar bond. Equations (47) and (48) are identical with equations we have obtained previously [3].

Let us now examine another limiting case:  $r_{AB} = \text{const}$ ,  $r_{AM} = \infty$ . In this case:

$$\alpha_M = \alpha', C_{AM} = \alpha_A + \alpha', C_{BM} = \alpha_B + \alpha', A_{AM} = A_{BM} = 0. \quad (49)$$

Equation 36 then takes the form:

$$4\beta'^2 (-1)^{l+m} \text{sh } \lambda \text{sh } \mu = 0, \quad (50)$$

and Equations (34) degenerate

$$\left. \begin{aligned} -X2\beta'(-1)^l \operatorname{sh} \lambda'' &= 0 \\ -Y2\beta'(-1)^m \operatorname{sh} \mu'' &= 0 \end{aligned} \right\} \quad (51)$$

whence

$$\text{either } \lambda'' = 0, \mu'' \neq 0, \text{ so that } Y = 0 \quad (52a)$$

$$\text{or } \lambda'' \neq 0, \mu'' = 0, \text{ so that } X = 0 \quad (52b)$$

and therefore, in accordance with (35), the local levels disappear altogether: the level  $W_1$  merges with energy zone (30), and the level  $W_2$  with the energy zone (32). In this limiting case, in accordance with (44) and (52a), the wave function (43) corresponding to the level  $W_1$  takes up the form:

$$\Psi_1 = X_1 \sum_g (-1)^{l,g} (\Phi_{pnpg} - \Phi_{nppg}), \quad (53)$$

which corresponds to a bond between the atoms A and B and absence of bonds with the lattice.

## 5. Discussion of Results

As we have seen, the solution of our problem leads to states of two types.

I. States (31) and (33) characterized by real values of the quasi-impulse. Corresponding to these states we have the energy levels (30) and (32), which form continuous bands (surface conductivity zone). In these states the electron of the lattice remains free.

II. States characterized by complex values of the quasi-impulse. States (43) are of this type, and to these states correspond the local energy levels (41). In this case the electron of the lattice is localized around the point of the surface which the molecule AB is approaching (Fig. 1).

Figure 2 is a diagrammatic representation of the energy of the system  $W$  as a function of the parameters  $r_{AB}$  and  $r_{AM}$  for different states of the system. The upper, shaded region in Fig. 2 refers to the states (31), and the lower, bold curve corresponds to the state (43) (for  $k = 1$ ). In Figure 2a, the abscissa is the reaction coordinate  $s$  ( $r_{AM}$  increases from right to left, and  $r_{AB}$  from left to right). Figure 2b refers to the case  $r_{AB} = \infty$ , i.e., when the atom is infinitely far removed. Here the abscissa is  $r_{AM}$ .

Let us examine Figure 2a. We see that the approach of the molecule AB to the crystal results in the formation of a local level  $W_1$ , which splits away from the surface conductivity zone  $W_\lambda$ ; the distance between this level and the zone increase as the molecule AB approaches still closer. In other words, the free electron of the lattice, which belongs to the surface conductivity zone of the crystal when the molecule AB is infinitely far removed, becomes localized on the surface under the influence of the approaching molecule; moreover, localization occurs around the point which the molecule AB is approaching and it increases in degree as the molecule becomes nearer.

As we move from left to right in Fig. 2a, the energy  $W_\lambda$  increases continuously. This means that the state (31) does not lead to adsorption. The energy  $W_1$ , however, passes through a maximum. If the curve  $W_1$  in the right part of Fig. 2a is lower than the lower limit of the  $W_\lambda$  band in the left part of the figure (as it is represented to be in Fig. 2a), this means that the state (43) (for  $k = 1$ ) results in adsorption (the usual exothermic adsorption).

The left part of Fig. 2a corresponds to the state  $AB + eL$ , in which  $eL$  is a symbol for the free electron in the lattice. In this initial state we have a free molecule AB and a free electron in the surface conductivity zone of the crystal. The right branch of the curve  $W_1$  (lower, bold curve) corresponds to the state  $B + AeL$ . In this final

state atom B is free (i.e., the bond between atoms A and B is broken), and atom A is bound to the surface by a "strong" homopolar (two-electron) bond in which a valence electron of the atom A and an electron of the lattice take part [3].

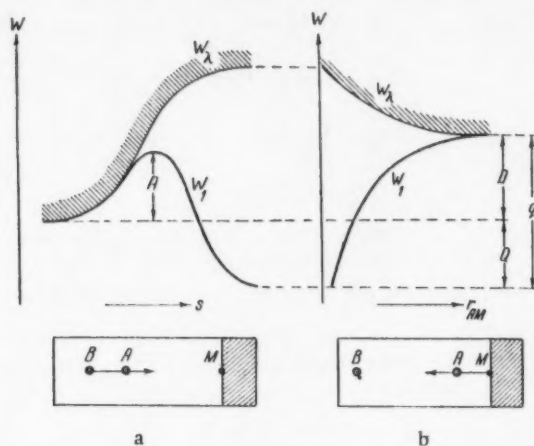


Fig. 2

We see that, as the molecule AB approaches the crystal, i.e., as the distance  $r_{AM}$  between atom A and the surface diminishes, the distance  $r_{AB}$  between atoms A and B increases. Hence, as the bond between atom A and the lattice increases in strength, the bond between the atoms A and B forming the molecule becomes weaker. This process, as will be seen from Fig. 2a, is associated with the surmounting of a certain energy barrier. The summit of the barrier corresponds to the state  $ABeL$ , an unstable transition state in which the atom A is bound both to B and to the lattice. The bonds formed in such a case are completely analogous to those formed in the molecule  $H_3$ .

Let us now turn to Fig. 2b, in which the energy of the system is represented as a function of  $r_{AM}$  for  $r_{AB} = \infty$ . The curve  $W_1$  in the left part of the figure corresponds to the state  $B + AeL$ . With increase in  $r_{AM}$  the level  $W_1$  approaches the conductivity zone and merges with it when  $r_{AM} = \infty$ . In other words, the localized electron of the lattice which effects the link between the atom A and the lattice is gradually delocalized as  $r_{AM}$  increases; the bond between A and the lattice becomes weaker, and in the limit, when  $r_{AM} = \infty$ , this bond is broken and the electron of the lattice is completely delocalized, i.e., is returned to the family of free electrons. We arrive at the state  $B + A + eL$ .

Hence, movement from left to right along the lower curve of Fig. 2 corresponds to the following succession of reactions:



In Figure 2,  $Q$  and  $q$  are the heats of reaction for (54a) and (54b), respectively;  $A$  is the activation energy for the reaction (54a);  $D$  is the dissociation energy of an isolated AB molecule.

As will be seen, our problem of the dissociation of a molecule AB on adsorption at the surface of an ionic crystal is quite analogous to the well known problem of Slater [4], who considered three univalent atoms A, B, and C arranged in a straight line and investigated the substitution reaction:



In our problem the part of the atom C is played by the crystal, regarded as a whole. Here, the free electron of the lattice fulfills the function of a free valence. This free valence wandering over the surface of the crystal,

brings about the rupture of the valence bond within the molecule AB and becomes saturated by the now freed valence of the atom A. This results in the adsorption of the atom A and, at the same time, to localization of this wandering valence.

The crystal surface here plays the part of a free radical, and the dissociation reaction occurring on adsorption may be written as an ordinary reaction occurring with the participation of a free radical:



In which L is the symbol for the lattice, and the dot over a letter denotes a free electron.

#### SUMMARY

1. An examination is made of the problem of the adsorption on an ionic crystal of a diatomic molecule formed from atoms which each have one valence electron. It is shown that, on adsorption, the free electron of the lattice becomes localized on a positive ion, which serves as an adsorption center.
2. It is shown that this localization of a free electron leads to rupture of the valence bond between the atoms forming the molecule and also to the simultaneous formation of a valence bond between one of these atoms and one of the atoms of the lattice (a "stable" homopolar bond).
3. This mechanism of adsorption accompanied by dissociation is shown to require a certain activation energy.

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## DEHYDROGENATION OF BUTANE-BUTENE MIXTURES INVESTIGATED WITH THE AID OF C<sup>14</sup>

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The manufacture of synthetic rubber from raw material not required for the production of food— in particular, from petroleum gases by dehydrogenation— becomes more and more of practical importance. The preparation of butadiene by dehydrogenation of butene over catalysts containing chromium oxide was studied in detail by Balandin, Bogdanova and Shcheglova [1, 2]. In this work a method of investigation was developed, the kinetics of the reaction were studied, the kinetic equation was found, and relative adsorption coefficients were determined for the reaction products and other substances, used as diluents for the butene.

In the work of Pshezhetsky, Lyubarsky, and co-workers [3, 4], this reaction was investigated at low temperatures and low conversions; these results were in accord with those of the investigations cited above [1, 2]. The dehydrogenation of butane to butene was also investigated [5, 6]. The kinetics of both reactions are characterized by considerable retardation by the reaction products, in the first case (dehydrogenation of butene) by butadiene, and in the second case by butene.

The dehydrogenation of the butane-butene mixtures formed by the dehydrogenation of butane presents great interest. Under the conditions of the dehydrogenation of butene these mixtures can give high yields of butadiene [7]. In this connection it is of interest to determine the relative rates of the dehydrogenation of butane and butene, whether in the dehydrogenation of the mixtures butadiene is formed directly from butane, and some other such facts. Since, in the dehydrogenation of the mixtures, butene is an intermediate product and yet at the same time a component of the original mixtures, the resolution of these questions by the usual methods did not appear to be possible. We used the isotopic-kinetic method proposed by Neiman [8], which has given good results in the investigation of homogeneous reactions, but has not been applied previously to the investigation of heterogeneous catalytic reactions, for which it has certain limitations: processes occurring entirely at a surface without liberating reaction products formed in separate elementary stages into the gas phase are at the limits of the sensitivity of the method. In the application of this method we used hydrocarbons (butane and butene) labeled with radioactive carbon C<sup>14</sup>.

### EXPERIMENTAL

#### Experimental Procedure

In the mixtures taken for dehydrogenation, butane and butene were taken in the ratio of 1:1. One of the gases was labeled with C<sup>14</sup>: in one series of experiments the butene was labeled, and in another series the butane was labeled. This procedure made it possible to compare the results and check them against one another.

Gas from a graduated gas holder was passed to a saturator [2], from which, diluted with water vapor in a molar ratio of 1:9, it passed to the reactor. The reaction products passed through a condenser, in which water vapor condensed, and were collected in a gas holder over saturated brine. Experiments were carried out with 2 ml of chromium oxide catalyst at 635°, the rate of passage of the butane-butene mixture being varied from 1000 to 5000 liters per liter of catalyst per hour, which corresponds to a variation of time of contact from 0.7



to 3.2 seconds. The time of contact was taken to be the reciprocal of the space velocity of passage of the butane-butene mixture (STP). During the work, the activity of the catalyst was frequently checked, and it was always the same.

In work with substances containing radioactive carbon, the brine in the gas holders was carefully blown out with air after each experiment in order to avoid contamination with radioactivity from the gases of previous experiments. In order to determine the radioactivity of the reactants and products, they were burnt [10] and the carbon dioxide formed was absorbed in baryta water. The precipitate was washed and centrifuged and was then transferred to an aluminum foil target [10]; its radioactivity was determined with the aid of an end-on counter.

In the case of the original substances, activity measurements were made on the butane, the butene dibromide obtained by passing the gas mixture through bromine at 0° (see below), and the mixture itself. In order to determine the radioactivity of the reaction products, part of the gas obtained in the experiment was passed through a barium hydroxide solution, when the carbon dioxide present gave a precipitate of barium carbonate. The gas was then fractionated in a Podbielniak apparatus and yielded a C<sub>1</sub>-C<sub>3</sub> fraction and a C<sub>4</sub> fraction consisting of butane, butene, and butadiene. The C<sub>1</sub>-C<sub>3</sub> fraction was separated by the thermochromatographic method in a stream of air in a column containing silica gel (ShSM brand). The pure hydrocarbons isolated were burnt to carbon dioxide, the radioactivity of which was determined as indicated above.

For the radiochemical analysis of butane, butene, and butadiene, the  $C_4$  fraction of hydrocarbons was brominated by the procedure used for the determination of butadiene in materials used for the manufacture of synthetic rubber [11], with some modifications. The mixture of gases was passed slowly into a small flask containing an excess (about 50%) of bromine. During bromination the gas in the flask was cooled with ice water. The outgoing gas was passed through a wash bottle containing caustic alkali solution to absorb bromine vapor and was then collected in a gas holder. In this way the fraction yielded butane and a mixture of the bromides of butene (dibromide) and butadiene (tetrabromide). Butane was further purified from unsaturated hydrocarbons by treatment with sulfuric acid and then burnt.

Butene dibromide was separated from butadiene tetrabromide by distillation at reduced pressure. Traces of bromide remained in both bromides, giving them an orange color. In order to purify it from bromine and dibromide, crystalline butadiene tetrabromide was recrystallized from ethanol. White needles, m.p. 116°, were obtained.

Found %: C 12.96; H 1.65; Br 85.48  $C_4H_6Br_4$ . Calculated %: C 12.95; H 1.61; Br 85.44

Redistillation of the dibromide gave a colorless or yellowish liquid.

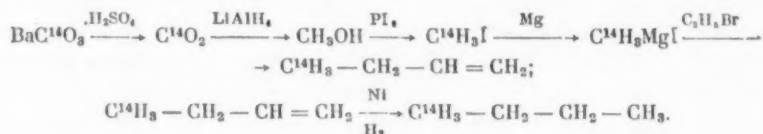
Found %: C 22.11; H 3.83; Br 74.21  $C_4H_8Br_2$ . Calculated %: C 22.39; H 3.73; Br 73.88

In this way the three hydrocarbons of the  $C_4$  fraction were isolated separately—the butane as such, and the butene and butadiene in the form of bromides.

### Starting Materials

The inactive butane and 2-butene used in the experiments were obtained from the works in the cylinders; they had been purified in the works in the large-scale rectification columns. The butane was further purified from unsaturated hydrocarbons by washing with concentrated sulfuric acid. The purity of the butane was specially determined and found to be 99.5%. The butene was purified with aminoniacal cuprous chloride and then refractionated through columns to purify it from light fractions; the purity of the butene was 98.8%.

Butene and butane labeled with radioactive carbon were synthesized as follows [12-15]:



The butane and butene so obtained were diluted with the inactive hydrocarbons and purified by three distillations through a Podbielniak column.

Two mixtures were prepared for the experiments: Mixture 1 was used in Experiments 16-20, and Mixture 2 was used in Experiments 21-23.

The characteristics of the mixtures were as follows.

Mixture 1: activity of butane 0; activity of mixture  $102 \pm 4$  impulses/minute  $\cdot$  mg; activity of butene  $205 \pm 4$  impulses/minute  $\cdot$  mg; composition of mixture - butene 50.5%, butane 49.5%.

Mixture 2: activity of butene 0; activity of mixture  $502 \pm 8$  impulses/minute  $\cdot$  mg; activity of butane  $1034 \pm 15$  impulses/minute  $\cdot$  mg; composition of mixture - butene 51.5%, butane 48.5%.

### Experimental Results and Discussion

1. Table 1 gives the results of the determination of specific activities in experiments with differing times of contact. For convenience of comparison of the results of Experiments 17-20 and Experiments 21-23, the relative values (%) of the specific activities are always given. The specific activity of 1 millimole of original gas (butene or butane) is taken as 100%.

TABLE 1

Specific Activities of Products \* per Millimole (% of original activity)

$\tau$ (seconds)	Experiment No.									
	Original gas	17	19	18	16	20	Original gas	22	23	21
	—	0.74	1.20	1.89	2.32	3.22	—	1.11	1.74	2.56
Product	Specific activity (%)									
CH <sub>4</sub>	—	—	33.5	—	—	32.0	—	5.03	8.5	5.95
C <sub>2</sub> H <sub>4</sub>	—	—	15.7	—	—	32.0	—	22.2	25.2	23.2
C <sub>2</sub> H <sub>6</sub>	—	—	—	—	—	—	—	—	—	—
C <sub>3</sub>	—	—	18.0	—	—	24.7	—	31.1	24.6	26.1
C <sub>4</sub> H <sub>6</sub>	—	97.0	98.5	98.5	97.0	99.4	—	0.39	0.29	0.48
C <sub>4</sub> H <sub>8</sub>	100	100.5	98.0	98.0	100.0	95.4	0	0.48	0.77	0.97
C <sub>4</sub> H <sub>10</sub>	0	0.5	0.5	0.5	0.75	1.15	100	99.8	99.7	98.8
CO <sub>2</sub>	—	35.0	32.2	33.8	—	33.4	—	0.69	0.46	0.57

\* Root mean square errors: in Experiments 16-20 for C<sub>4</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>6</sub>, and CO<sub>2</sub>—1.6%, for C<sub>4</sub>H<sub>10</sub>—37%; in Experiments 21-23 for C<sub>4</sub>H<sub>8</sub>—4.7%, for C<sub>4</sub>H<sub>6</sub>—15%, for C<sub>4</sub>H<sub>10</sub> and CO<sub>2</sub>—1.3%. Considerable errors are obtained only when the activities are very low.

Figure 1, which shows the dependence of the specific activities of butane, butene and butadiene on time of contact, is based on the data of Table 1. In Experiments 16-20 the specific activities of butene and butadiene are almost identical (Fig. 1a). If an appreciable amount of butadiene were formed directly from butane without passing through the stage of the formation and desorption of butene, then for the mixture of butene-C<sup>14</sup> and butane, the butadiene should have lower specific activity than the butene.

On the other hand, in Experiments 21-23 with a mixture of butane-C<sup>14</sup> and butene, which were carried out with great accuracy, formation of butadiene directly from butane should increase the specific activity of butadiene with respect to butene. In Fig. 1b, we have the reverse picture: the specific activity of butadiene is lower than that of butene.

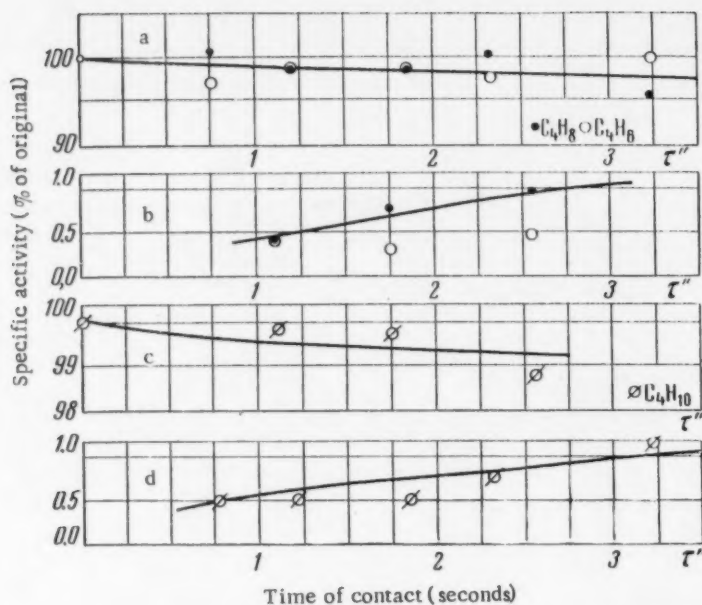
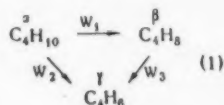


Fig. 1. Relation of specific activity to time of contact: a) butene and butadiene in Experiments 16-20; b) butene and butadiene in Experiments 21-23; c) butane in Experiments 21-23; d) butane in Experiments 16-20.

Such a relationship should hold if, in the scheme



( $w_1$ ,  $w_2$ , and  $w_3$  are rates of reaction,  $\alpha$ ,  $\beta$ , and  $\gamma$  are the specific activities of butane, butene, and butadiene)  $w_2 \ll w_3$ .

Using the isotopic-kinetic method [8] we may write for the rate of formation of butadiene ( $c_1$  is the concentration of butadiene):

$$\frac{dc_1}{d\tau} = w_2 + w_3,$$

and for the rate of accumulation of activity in butadiene:

$$\frac{dc_1^*}{d\tau} = w_2^* + w_3^*, \text{ where } w_3^* = \beta w_3, \quad w_2^* = \alpha w_2, \quad c_1^* = \gamma c_1.$$

Differentiating the last equation, we obtain:

$$\frac{dc_1^*}{d\tau} = \frac{d\gamma}{d\tau} c_1 + \frac{dc_1}{d\tau} \gamma.$$

Neglecting  $w_2$ ,  $\beta w_3 = \frac{d\gamma}{d\tau} c_1 + \frac{dc_1}{d\tau} \gamma$ , so that  $\frac{d\gamma}{d\tau} = \frac{(\beta - \gamma) w_3}{c_1}$ .

If the specific activity of butadiene increases with time ( $d\gamma/d\tau > 0$ ), then its specific activity should be less than that of butene ( $\beta > \gamma$ ). As will be seen from Fig. 1b, such a picture was observed even in Experiments 21-23. Hence, in the dehydrogenation of butane-butene mixtures under the above-described conditions, the formation of butadiene proceeds by the dehydrogenation of butene and practically no conversion of butane directly into butadiene occurs.

2. As butadiene is formed almost entirely from butene that comes to the catalyst from the gas phase and not from the butene remaining on the catalyst (which is formed from butane and then not desorbed from the catalyst), we can make some further inferences. Figure 2 shows a diagrammatic representation of the potential profile of the process. Part I of Fig. 2, which is to the left of the vertical AB, refers to the dehydrogenation of butane; Part II, which is to the right of AB, refers to the dehydrogenation of butene on the active surface of the catalyst. Here 1 is the energy level of the original butane molecule; 2 is the level of the butane molecule adsorbed on the active surface; 3) is the level of the activated multiplet complex in the dehydrogenation of butane to butene; 4 is the level of the adsorbed butene molecule; 5 is the level of the butene molecule desorbed from the catalyst surface into the gas.

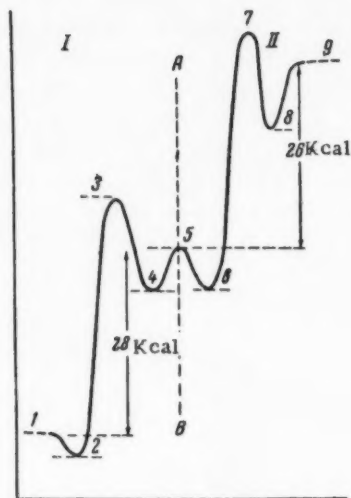


Fig. 2. Potential profile for the process of stagewise dehydrogenation of butane into butene and butadiene.

The difference in the levels 1 and 2 is the energy of adsorption of butane; the difference 1-5 (endothermic) is the heat of the dehydrogenation reaction; the difference 4-5 is the energy of desorption of butene. In Part II, level 5 is the energy of butene in the gas, and level 6 is the energy of adsorbed butene (as the level of butene in the gas is the same in Reactions I and II, it is indicated by 5 in each case). Level 7 is the level of the activated multiplet complex of the catalytic dehydrogenation of butene; 8 is the level of adsorbed butadiene, and 9 is the level of butadiene in the gas. The difference 5-6 is the energy of adsorption of butadiene, 5-9 is the heat of dehydrogenation of butene, and 8-9 is the energy of desorption of butadiene.

The experimental results described above indicate that the rate constant for desorption of butene  $k_{45}$  in Part I is greater than the rate constant for dehydrogenation of butene  $k_{57}$  in Part II, i.e.,

$$k_{45} > k_{57}. \quad (1)$$

In Part II, the rate constant for adsorption of butene  $k_{56}$  should be greater than that for its desorption  $k_{65}$ . Actually, the equilibrium constant for the adsorption of butene  $K$  is given by

$$K = \frac{[C_4H_8 \cdot S]}{[C_4H_8][S]},$$

In which  $S$  represents atoms of the surface. As the kinetics show, under dehydrogenation conditions the surface is almost completely covered, i.e.,  $[C_4H_8 \cdot S]$  is close to 1 and  $[S]$  is close to 0; hence  $K > 1$ , and as  $K = k_{56}/k_{65}$ , therefore

$$k_{56} > k_{65}. \quad (2)$$

However, it is obvious that the level of adsorbed butene is the same in Reactions I and II, and therefore

$$k_{65} = k_{45}. \quad (3)$$

Comparing (1), (2) and (3), we find that

$$k_{56} > k_{65} > k_{57}. \quad (4)$$

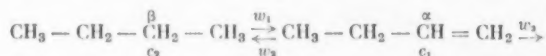
Hence, the rate constants for the adsorption and desorption of butene are higher than that for its dehydrogenation, so that adsorption equilibrium should be established rapidly as compared with the rate of the dehydrogenation reaction.

This result is important in principle for the kinetics of dehydrogenation: the interpretation of the constants of the kinetic equations for dehydrogenation given previously by one of us [16] is now confirmed by the method of labeled atoms. The result obtained here for an oxide catalyst is in accord with results obtained for the metal catalyst osmium [17]. It may be considered, therefore, that this relationship between the rate constants for adsorption and desorption is true for all dehydrogenation reactions [18]. This does not indicate that other relationships between the constants do not hold for reactions of other types.

In order to obtain the result found, study of the successive reactions was important, because Equation 3 must necessarily hold. The lower position of maximum 456 as compared with maximum 678 is in accordance with the facts in the following respect. The height of the desorption barrier  $Q_{66}$  should be considerably less than that of the barrier  $Q_{67}$ , because  $Q_{67}$  should be fairly close to the heat of the dehydrogenation of butene to butadiene,  $Q_{59} = 26$  kcal/mole, whereas the energy of desorption of butene should be considerably lower, scarcely exceeding 10 kcal/mole. Then if the rate constant is the higher, the lower the energy barrier, we shall obtain the exact relationship of constants as is found experimentally.

3. It will be seen from Table 1 and Fig. 1 that the specific activity of the labeled component of the mixture diminishes with increase in time of contact (butene in Experiments 16-20, and butane in Experiments 21-23). It is clear that for butene this is readily explained by the dehydrogenation of butane, and for butane it is readily explained by the hydrogenation of butene.

An attempt at a quantitative treatment of the data of Table 1 and Fig. 1 gave a somewhat unexpected result. By the application of the isotopic-kinetic method to the following reaction scheme:



( $\alpha$  and  $\beta$  are the specific activities of butene and butane, and  $c_1$  and  $c_2$  are their concentrations), it is not difficult to obtain an equation for the rates of dehydrogenation of butane and hydrogenation of butene ( $w_1$  and  $w_2$ ).

It will be clear that for butene the rate at which the concentration changes will be  $dc_1/d\tau = w_1 - w_2 - w_3$ , and the rate of change of radioactivity will be  $dc_1^*/d\tau = w_1^* - w_2^* - w_3^*$ , in which  $c_1^* = \alpha c_1$ , and  $w_1^* = \alpha w_1$ , etc.

We then have  $dc^*/d\tau = dc_1/d\tau \beta + d\beta/d\tau c_1$  and  $w_1 = d\beta c_1/d\tau (\beta - \alpha)$ . Similarly we can obtain

$$w_2 = d\alpha c_1/d\tau (\beta - \alpha).$$

For the determination of the rates  $w_1$  and  $w_2$ , the values of  $\alpha$ ,  $\beta$ ,  $d\alpha/d\tau$  and  $d\beta/d\tau$  were determined graphically from Fig. 1. The concentrations  $c_1$  and  $c_2$  were calculated from data on the percentage composition of the gas, obtained in a special series of experiments. These data, recalculated for Experiments 16-23, are given in Table 2.

The results of the calculations of the rates  $w_1$  and  $w_2$  are given in Table 3.

From Table 3 it will be seen, first, that for experiments with different mixtures (butane- $\text{C}^{14}$  + butene and butene- $\text{C}^{14}$  + butane) the values of  $w_1$  and  $w_2$  are in close agreement and, second, that the rate of dehydrogenation of butane is almost equal to, and does not exceed, the rate of hydrogenation of butene, although under the experimental conditions thermodynamic equilibrium is displaced by 90% in the direction of the dehydrogenation of butane [6, 7].



TABLE 2

Amounts of Products (millimoles per liter of original gas) (root mean square error  $\pm 2\%$ )

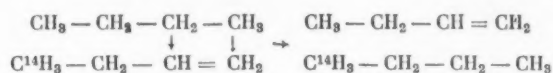
Substance	Experiment No.								Original gas
	17	19	18	16	20	22	23	21	
CH <sub>4</sub>	0.56	0.76	1.03	1.07	1.17	0.72	0.96	1.10	—
C <sub>2</sub> H <sub>4</sub>	0.49	0.54	0.58	0.61	0.65	0.54	0.56	0.63	—
C <sub>2</sub> H <sub>6</sub>	0.77	1.68	2.11	2.35	2.64	1.61	2.06	2.46	—
C <sub>3</sub>	0.63	0.85	1.21	1.39	1.66	0.81	1.14	1.48	—
C <sub>4</sub> H <sub>6</sub>	5.55	6.50	7.25	7.75	9.00	6.28	7.10	8.10	—
C <sub>4</sub> H <sub>8</sub>	14.7	13.9	13.0	12.9	12.3	14.1	13.0	13.0	22,35
C <sub>4</sub> H <sub>10</sub>	22.1	21.9	21.5	21.2	20.5	21.9	21.6	21.0	22,35
CO <sub>2</sub>	2.24	3.02	3.85	4.04	4.56	2.89	3.72	4.33	—

TABLE 3

Reaction Rates for the Hydrogenation of Butene and Dehydrogenation of Butane (millimoles per second per liter of original gas)

$\tau$ sec.	$c_1$ mm/ liter	$c_2$ mm/ liter	For experiments 16-20					For experiments 21-23				
			$-(\alpha-\beta)$	$\frac{d\alpha}{d\tau}$	$-\frac{d\beta}{d\tau}$	$w_1$	$w_2$	$(\alpha-\beta)$	$\frac{d\beta}{d\tau}$	$-\frac{d\alpha}{d\tau}$	$w_1$	$w_2$
1.0	14.0	22.0	98.2	0.2	0.3	0.043	0.045	99.2	0.3	0.2	0.042	0.044
1.5	13.2	21.7	97.9	0.2	0.3	0.041	0.045	98.9	0.3	0.2	0.040	0.044
2.0	12.9	21.4	97.5	0.2	0.3	0.040	0.044	98.7	0.3	0.2	0.039	0.043
2.5	12.7	21.2	97.2	0.2	0.3	0.039	0.044	98.4	0.3	0.2	0.039	0.043
3.0	12.4	21.0	97.0	0.2	0.3	0.038	0.043	98.1	0.3	0.2	0.037	0.043

We consider that the following reaction occurs:



This is the new reaction of simultaneous catalytic hydrogenation and dehydrogenation of two molecules; it is allied to the reaction of disproportionation of hydrogen (so-called irreversible Zelinsky catalysis) in that two hydrogen atoms pass from two adjacent carbon atoms to two adjacent carbon atoms linked by a double bond in another molecule, for example for cyclohexene:



In the schemes given above such transitions of hydrogen atoms are denoted by arrows. However, in the new reaction there is an essential difference: if we neglect isotopic composition, the reaction products do not differ from the reactants. Hence, the isobaric potentials of reactant and reaction product must be identical, from which

by thermodynamic reasoning it follows that the equilibrium constant for this reaction at any temperature must be unity, so that, thermodynamically, reaction is possible both in the forward and in the reverse directions; the limiting degree of conversion should be 50%. In this respect, the new reaction is allied to isotopic exchange, in which we again have interchange of hydrogen atoms between two molecules. The degree of conversion (with respect to this reaction) observed in the present work is still far from the thermodynamic limit. The occurrence of this reaction removes the apparent contradiction with respect to the rate constants for dehydrogenation of butane and hydrogenation of butene (see above). It is scarcely necessary to mention that the occurrence of this reaction does not in any way affect the correctness of the conclusions reached in the first part of this section concerning the relationship between the rate constants of adsorption and catalysis for the dehydrogenation reaction.

TABLE 4

Total Activity of Products (for 1 liter of original gas— percent of original activity)

Product	Experiment No.									
	Original $C_4H_8$	17	19	18	16	20	Original $C_4H_{10}$	22	23	21
$CH_4$	—	—	1.14	—	—	1.68	—	0.16	0.37	0.29
$C_2H_4$	—	—	0.38	—	—	0.93	—	0.54	0.63	0.66
$C_2H_6$	—	—	—	—	—	—	—	—	—	—
$C_3$	—	—	0.69	—	—	1.84	—	1.13	1.26	1.73
$C_3H_6$	—	24.20	28.80	32.10	33.8	40.10	—	0.01	0.01	0.02
$C_4H_8$	100	66.30	61.20	57.3	57.9	52.70	—	0.03	0.05	0.06
$C_4H_{10}$	—	0.05	0.05	0.05	0.07	0.11	100	98.10	96.5	93.2
$CO_2$	—	3.52	4.36	5.84	—	6.82	—	0.01	0.01	0.01
Total	—	—	96.6	—	—	104.2	—	99.98	98.8	96.00

4. Tables 1 and 2 enable us to calculate the total radioactivity of the reaction products and construct a balance sheet for the radioactivity in a series of experiments. As such a balance sheet forms a characterization of the experimental material, it was considered desirable to give the results of these calculations. Table 4 gives radioactivities of reaction products as percentages of original activity.

It will be seen that the balance sheet of activities is satisfactory.

#### SUMMARY

1. It was shown that in the dehydrogenation of butane-butene mixtures over a chromium oxide catalyst the formation of butadiene proceeds by the dehydrogenation of butene; practically no direct conversion of butane into butadiene occurs.
2. It was found that the rate constant for the desorption of butene is greater than that for its dehydrogenation, a fact which is important in principle for the theory of dehydrogenational catalysis.
3. Results were obtained which indicate that a reaction of redistribution of hydrogen occurs between butane and butene, consisting in simultaneous hydrogenation of butene and dehydrogenation of butane proceeding together with the general dehydrogenation reaction. This new reaction is on the one hand allied to disproportionation of hydrogen, and on the other to isotopic exchange of hydrogen.

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PREPARATION OF 1,6-HEXANEDIAMINE BY HYDROGENATION  
OF ADIPONITRILE OVER A NICKEL CATALYST UNDER  
FLOW CONDITIONS

L. Kh. Freidlina, A. A. Balandin, K. G. Rudneva  
and T. A. Sladkova

1,6-Hexanediamine is an important component in the manufacture of polyamide resins from which high-quality synthetic fibers are prepared. It may be prepared by splitting sebacamide [1], by reaction of 1,6-dibromohexane with ammonia [2], from caprolactam [3], and by hydrogenation of butenedinitriles [4]. However, at the present time, the cheapest and most readily accessible raw material for the preparation of 1,6-hexanediamine is adiponitrile.

Adiponitrile may be reduced with active hydrogen obtained with the aid of sodium [5] or aluminum amalgam [6], or electrolytically, or with the aid of expensive platinum-palladium catalysts [7], but for various reasons all these methods are unsatisfactory for industrial use. Hydrogenation in presence of nickel and cobalt catalysts is more satisfactory, but this requires high pressure.

Silchenko and Krolik [8] hydrogenated adiponitrile in presence of Ni-Co-Al and Ni-Fe-Mg-Al alloy catalysts and obtained 1,6-hexanediamine in 70% yield. Arbuzov and Pozhiltsova [9] hydrogenated the dinitrile in a rotating autoclave in a butyl alcohol medium in presence of large amounts of Raney nickel (30-50% on the amount of dinitrile taken). Hydrogenation was carried out for three hours at 100° under a pressure of hydrogen of 60 atm in absence of ammonia; the yield of diamine was 83-85%. The following catalysts have been recommended in the patent literature for this reaction: cobalt [10], nickel-aluminum [11], nickel-alumina [12], Raney nickel promoted with chromium [13], and also the mixed catalyst Ni-Co-silica gel (1: 2: 3) [14].

Zilberman and Skorikova [15] studied the hydrogenation of adiponitrile in a rotating autoclave in presence of Raney nickel. They found that the optimum conditions are: temperature up to 140°, pressure above 75 atm, amount of catalyst about 10%, duration 30 minutes, and weight ratio of ammonia to nitrile 1.5 : 1. Under these conditions the yield of 1,6-hexanediamine was 80-85%.

It will be seen from the results cited from the literature that the catalytic hydrogenation of adiponitrile has been studied only under static conditions. We have now studied the hydrogenation of this compound over Raney nickel under flow conditions.

EXPERIMENTAL

Hydrogenation Apparatus. The apparatus is shown diagrammatically in the figure. It consists of the following main parts: 1.6-liter mixer with mechanical stirrer; four-stage gas compressor for feeding ammonia into the mixer; reactor ( $d = 21$  mm,  $l = 1150$  mm) heated by an electric furnace; multiplier with two working cylinders (capacity 90 ml each) for uniform feeding of the dinitrile-ammonia mixture into the reactor; receiver for the reaction products; gas compressor for compressing the hydrogen; two reservoirs, two hydraulic pumps; cylinders of hydrogen, nitrogen, and ammonia.

Experimental Procedure. The moist catalyst in the form of 3-7 mm grains was introduced into the reactor in a continuous spray of water. Broken porcelain (25 ml) was placed above the catalyst layer. The system was washed out with nitrogen and hermetically sealed. With the aid of the pump 1, the dinitrile was sucked

from a flask into the mixer 2. The mixer stirrer was set going, and ammonia was passed in from a cylinder by means of the compressor 16. The ammonia content of the mixture was determined in a test sample, which was run off into a solution of sulfuric acid and titrated with alkali in presence of a mixed indicator (Methyl red and Methylene blue) [16].

The mixture was pushed over into one of the two working cylinders of the multiplier 5 and 6 under a pressure of nitrogen. Hydrogen and the dinitrile-ammonia mixture was passed into the reactor 3 from above. The temperature in the reactor was measured with a thermocouple mounted in a metal pocket situated in the middle of the catalyst layer. The rate at which mixture from the working cylinder of the multiplier was fed into the reactor was controlled by varying the speed of the pump and was calculated from the rate at which oil flowed from the middle cylinder of the multiplier 8, taking account of the ratio of the squares of the diameters of the pistons of the middle and working cylinders of the multiplier. The consumption of hydrogen in the reaction was compensated by its supply from a reservoir.

The catalyst was prepared by leaching 40% of aluminum from a nickel-aluminum alloy containing 50% of nickel. Leaching was carried out with 20% sodium hydroxide solution at 100°. The carefully washed catalyst was kept under a layer of water. In the breaks between experiments the catalyst was kept in the reactor under a low pressure (2-3 atm) of hydrogen. Before being hydrogenated, the crude industrial dinitrile was purified by a distillation at a residual pressure of 25 mm, a fraction boiling over a range of 1-2° being taken. The reaction products were removed from the apparatus, weighed, and fractionated.

**Separation of Reaction Products.** The hydrogenation products were fractionally distilled in a stream of nitrogen. Fraction I, boiling up to 140°, contained hexamethylenimine, b.p. 138°, and some water. Fraction II came over at 95-110° (20 mm) and consisted of 1,6-hexanediamine [b.p. 200° (760 mm); 117° (50 mm); 100° (20 mm)]. Fraction III came over at 120-130° (20 mm) and was found to be 6-aminohexanenitrile [b.p. 200° (760 mm); 120° (20 mm)]. The residue consisted of higher-boiling reaction products (bis-hexamethylenetriamine) and unchanged dinitrile. The yields of the fractions were calculated on the total amount of reaction products. The amine values of the fractions were determined.

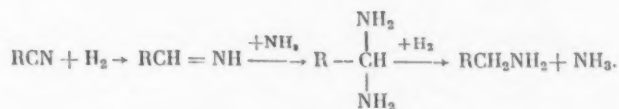
**Effect of the Length of the Catalyst Layer.** At first experiments were carried out with a catalyst layer 32 cm in length (95 ml). Under the optimum conditions for this sample (80°, hydrogen at 150 atm, 40% of ammonia in the original mixture) the yield of 1,6-hexanediamine was about 40%. Reduction of the space velocity of the dinitrile from 0.8 to 0.1 liter/liter · hour did not result in an increased yield of diamine. It might be supposed that constancy of yield of diamine irrespective of variation of pressure, temperature, and space velocity could result from insufficient time of contact between dinitrile and catalyst. Further experiments were therefore carried out with a catalyst layer of length 95 cm (300 ml). It will be seen from Table 1 that, with increase in the length of the catalyst layer the yield of 1,6-hexanediamine did in fact increase greatly, attaining 70%. Increase in the space velocity of passage of dinitrile from 91 to 188 g/liter · hour had no substantial effect on the yield of diamine. This indicated that the productivity of the catalyst was still only partially utilized under these conditions.

TABLE 1

Effect of Space Velocity (Experimental conditions: 80°, 150 atm, 55% of ammonia in original mixture)

Experiment	Space velocity of passage of dinitrile g/liter · hour	Composition of product (% weight of fractions)	
		II	III
1	95	70.0	10.0
2	91	63.2	7.6
3	188	56.3	2.5
4	137	65.8	2.3

**Effect of the Proportion of Ammonia admixed with the Dinitrile.** Schwogler and Adkins [17] showed that formation of secondary amines can be reduced by carrying out hydrogenation of nitriles in presence of a large excess of ammonia; they explain this as follows:

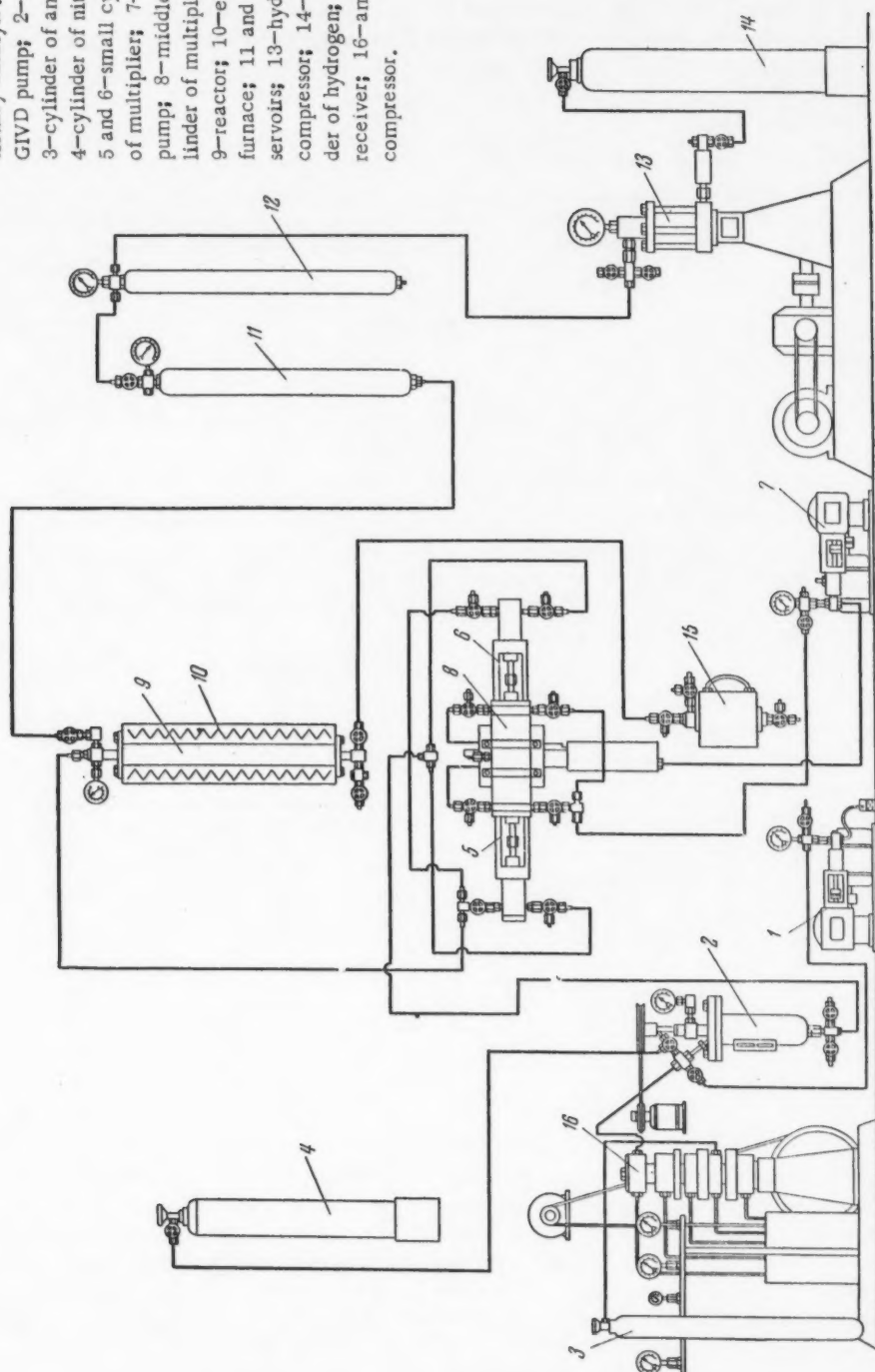


We found that, under our flow conditions, it is sufficient to add 15% by weight of ammonia to the dinitrile.

It will be seen from Table 2 that lowering of the ammonia content of the original mixture from 55 to 15% (Experiments, 3, 5, 7, and 8) has little effect on the extent to which the nitrile is hydrogenated. The yields of



Diagram of apparatus for the hydrogenation of adiponitrile over a stationary catalyst: 1—stationary catalyst; 2—mixer; 3—cylinder of ammonia; 4—cylinder of nitrogen; 5 and 6—small cylinders of multiplier; 7—GIVD pump; 8—middle cylinder of multiplier; 9—reactor; 10—electric furnace; 11 and 12—re-servois; 13—hydrogen compressor; 14—cylinder of hydrogen; 15—receiver; 16—ammonia compressor.



1,6-hexanediamine in these experiments were 59.0, 63.4, 62.6, and 56.4%, respectively. Lowering of the ammonia content of the mixture to 10% caused the yield of diamine fall to 42.0%, whereas the yield of the imine fraction rose to 28.7% (Experiment 6). In the next experiment—No. 7 with 15% of ammonia—the yield of 1,6-hexanediamine was 62.6%, i.e., the same as in Experiment 5, which indicates that the activity of the catalyst remains constant.

Effect of Temperature. It will be seen from Table 3 that in experiments at 80° the yield of 1,6-hexanediamine attains 69–79% and the yield does not increase when the temperature is raised to 100° (Experiment 11). With lowering of temperature to 60° the yield of 1,6-hexanediamine falls to 21.0%, the yield of the product of

TABLE 2

Effect of the Ammonia Content of the Original Mixture (Experimental conditions: 80°, 150 atm)

Experiment	Ammonia content of mixture (%) by weight	Space velocity of passage of dinitrile (g/liter · hr)	Composition of product (% by weight of fractions)			
			I	II	III	residue
3	55	188	16.8	59.0	4.0	21.2
5	15	201	16.2	63.4	3.5	16.9
6	10	248	28.7	42.0	1.0	28.3
7	15	224	8.2	62.6	2.2	27.0
8	25	178	13.1	56.4	1.0	29.5

Incomplete hydrogenation (Fraction III) rises to 41%, and the amount of unchanged dinitrile is 33% (Experiment 12). In the next experiment, at 80° (Experiment 13), the yield of 1,6-hexanediamine is 69.2%, i.e., the catalyst has the same activity as it had before Experiment 12. Hence, the low yield of diamine at 60° is indeed due to the low temperature of the experiment.

TABLE 3

Effect of Temperature (Experimental conditions: 50 atm, 15–25% by weight of ammonia in mixture)

Experiment	Temperature (°C)	Space velocity of passage of dinitrile (g/liter · hr)	Composition of product (% by weight of fractions)			
			I	II	III	residue
9	80	202	7.8	76.9	1.0	14.3
10	80	198	7.6	78.9	1.0	12.5
11	100	197	12.3	68.5	1.0	18.2
12	60	178	5.0	21.0	41.0	33.0
13	80	198	12.8	69.2	10.6	7.4

Effect of Pressure. As will be seen from Table 4, the highest yield of 1,6-hexanediamine (79.6%) was obtained in the experiment at 50 atm. With increase of pressure to 100–150 atm (Experiments 14, 16, 7), the yield of diamine was somewhat lower, and at 200 atm the yield was considerably lower (Experiment 15). With lowering of pressure to 20 atm the yield of diamine fell to 22.5%; the yield of the incompletely hydrogenated product (the amino nitrile) increased (28.3%), and the residue contained much unchanged dinitrile (Experiment 17). We then carried out repeat experiments at 150 atm (Experiment 8) and 50 atm (Experiment 10). It was found that the catalyst retained its high activity, i.e., it did not undergo irreversible changes in the experiment at 200 atm.

Stagewise Character of the Hydrogenation of Adiponitrile. As Arbuzov and Pozhiltsova [9] showed, when the pressure is lowered to 0.5-0.7 atm, only incomplete hydrogenation to 6-aminohexanenitrile occurs. Under our flow conditions; with lowering of pressure to 20 atm the yield of Fraction III rose to 28.3% (Experiment 17). A large amount of the amino nitrile was formed also in Experiment 12, in which the hydrogenation was carried out at the comparative low temperature of 60°. Increase in the yield of the amino nitrile was observed also in

TABLE 4

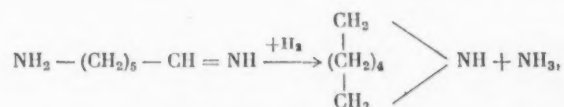
Effect of Pressure (Experimental conditions: 80°, 15-25% by weight of ammonia in mixture)

Experiment	Space velocity of passage of dinitrile (g/liter hour)	Pressure (atm)	Composition of product (% by weight of fractions)			
			I	II	III	residue
7	224	150	8.2	62.6	2.2	27.0
14	198	100	8.6	68.6	3.7	19.1
15	177	200	16.2	33.4	1.0	49.4
16	196	100	8.7	68.4	2.7	20.2
9	202	50	7.8	76.9	1.0	14.3
17	178	20	6.6	22.5	28.3	42.6
8	178	150	13.1	56.4	1.0	29.5
10	198	50	7.6	78.9	1.0	12.5
13	198	50	12.8	69.2	10.6	7.4

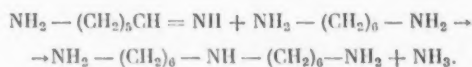
experiments with insufficient catalyst carried out under static conditions [15]. These facts show that the hydrogenation of adiponitrile has a stagewise character and the first nitrile group is hydrogenated more readily than the second. In spite of the short time of contact between the substance to be hydrogenated and the catalyst under flow conditions, we succeeded in hydrogenating as much as 80% of the dinitrile to the diamine.

Causes of Side Reactions. Under the conditions of the flow system, the ratio of the amounts of catalyst and dinitrile in the sphere of reaction at any given moment is much greater than in liquid-phase hydrogenation over a catalyst in powder form. This fact and the high activity of the Raney catalyst enabled us to reduce the duration of the hydrogenation of the dinitrile very greatly and lower the reaction temperature to 80-100°. Both factors—low temperature and continuous removal of products from the sphere of reaction—reduced the possibility of the formation of by-products from side reactions and favored a high yield of 1,6-hexanediamine. However, even in these very mild conditions, side reactions occurred with formation mainly of hexamethylenimine and bis-hexamethylenetriamine.

It may be suggested [18] that hexamethylenimine is formed from an intermediately formed aldimine:

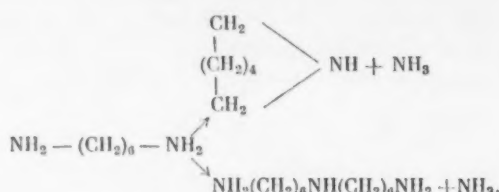


and bis-hexamethylenetriamine—by reaction of the aldimine with the diamine:



With rise of temperature and increase in the time of contact with the catalyst, by-products can be produced

also in the process of deamination of the 1,6-hexanediamine formed:



The formation of secondary amines as products of side reactions is associated with the nature of the active surface of the catalyst. It would appear that a cobalt catalyst is to be preferred in this respect to a nickel catalyst, since a smaller amount of secondary amines is formed when it is used [19].

The effect of the alkalinity of the medium is also of interest. It will be seen from Table 5 that, when a solution of 0.16 g of sodium hydroxide in 20 ml of water is introduced into a mixture of the dinitrile (481 g)

TABLE 5

Effect of Addition of Alkali (Experimental conditions: 80°, 50 atm)

Experiment	Space velocity of passage of dinitrile (g/liter hour)	Amount of sodium hydroxide in mixture (%) by weight	Composition of product (% by weight of fractions)			
			I	II	III	residue
18	174	—	10.0	75.2	2.5	12.3
19	165	0.03	10.5	74.3	2.2	13.0
20	216	0.24	39.4	34.4	10.0	16.2
21	187	—	16.2	48.5	16.3	19.0

and ammonia (25% by weight), the yields of diamine (74.3%) and imine (10.5%) do not differ from those obtained in absence of water and alkali (Experiments 18 and 19). When a solution of 1 g of sodium hydroxide in 20 ml of water is added to a mixture of the dinitrile (425 g) and ammonia (20%), the yield of imine rises sharply to 39.4%, and the yield of 1,6-hexanediamine falls correspondingly to 34.4% (Experiment 20). The next experiment (Experiment 21), in which no alkali was added showed that, after the experiment with alkali, the activity of the catalyst fell appreciably: the yield of 1,6-hexanediamine fell to 48.5%.

Zilberman and Skorikova [15] found that addition of water (up to 11%) or adipamide (up to 5%) to the dinitrile-ammonia mixture does not affect the yield of diamine, but addition of 0.5% of ammonium adipate reduces the yield.

**Mechanical Strength of Catalyst.** One cause of the gradual reduction of the yield of 1,6-hexanediamine during the process may be reduction in the activity of the catalyst owing to mechanical disruption of its surface layer. In our experiments under optimum conditions the amount of nickel particles carried away was small, but became considerable in experiments at higher temperatures (120-150°), at higher pressures (200 atm), and at higher concentrations of ammonia in the dinitrile-ammonia mixture. Disruption of the active layer of catalyst under these conditions is probably to be explained by the more rapid chemical interaction of its highly dispersed particles with hydrogen, ammonia, and amines.

## SUMMARY

1. The effect of various factors on the hydrogenation of adiponitrile in a flow system under pressure was investigated.

2. It was shown that, under flow conditions with a sufficiently long layer of catalyst, adiponitrile is hydrogenated with formation of 1,6-hexanediamine in high yield (ranging to 80%).

3. The high activity of the Raney nickel catalyst and the high ratio of the amounts of catalyst and of dinitrile undergoing hydrogenation make it possible to carry out the process under mild conditions (temperature 80°, pressure of hydrogen 50 atm).

4. Lowering of the temperature to 60° and of the pressure to 20 atm leads to a reduction in the yield of the diamine and an increase in the yield of the product of incomplete hydrogenation, 6-aminohexanenitrile. Raising the temperature and pressure favors side reactions and accelerates the deactivation of the catalyst.

5. Addition of 0.24% of sodium hydroxide to the dinitrile leads to a great reduction in the yield of diamine and to an increase in the yield of hexamethylenimine.

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KINETICS AND CHEMISTRY OF THE POLYCONDENSATION OF  
 $\alpha$ -AMINO ESTERS

COMMUNICATION 2. KINETICS OF THE POLYCONDENSATION  
OF GLYCINE ETHYL ESTER \*

Yu. I. Khurgin, K. T. Poroshin and T. D. Kozarenko

The polycondensation of  $\alpha$ -amino esters is one of the most widely used methods for the preparation of peptides. On the basis of this reaction, taken as typical of polycondensation processes, important laws governing such processes can be derived. Moreover, study of the polycondensation of  $\alpha$ -amino esters enables us to make an approach to the solution of the problem, important from the biochemical point of view, of determining the mechanism of the formation (synthesis) of the peptide link. It is known that the synthesis of peptides by polycondensation is a catalytic reaction. The synthesis of peptides from  $\alpha$ -amino esters proceeds in presence of various proteolytic enzymes [1]. On the other hand, we have previously demonstrated the initiating effect of various acidic substances on the polycondensation of  $\alpha$ -amino esters [2]. Among acidic initiators, carbon dioxide is of special interest [2, 3].

Progress of polycondensation is most clearly indicated by the change in content of end groups and by the rate at which monomer is exhausted. We have previously investigated the kinetics of the polycondensation of alanine [2] and glycine [3] by measuring the rate at which the content of terminal amino groups diminished. With rise in temperature and in initial concentration of carbon dioxide ( $\xi_0$  changed from 0.05 to 0.03) the rate of polycondensation increased, although the form of the kinetic curves did not change. In the preceding communication [4] we studied the kinetics of the change of composition of the polycondensation products of glycine ethyl ester in presence of a constant initial amount of carbon dioxide ( $\xi_0 = 0.02$ , in which  $\xi_0 = [\text{CO}_2]_0/M_0$ —the ratio of the initial molar concentrations of carbon dioxide and glycine ethyl ester). The rate at which glycine ethyl ester enters the polycondensation follows a first-order equation with a rate constant of  $k = 5.85 \cdot 10^{-5} \text{ sec.}^{-1}$  [4].

The present work was undertaken with the object of studying the effect of the initial concentration of carbon dioxide  $\xi_0$  and temperature on the progress of polycondensation of glycine ethyl ester ( $\xi_0 = 0.01, 0.02, 0.04, 0.08$  and  $0.16$ ). As the main index of progress of polycondensation we took the amount of monomer removed from the medium by reaction. We also investigated the effect of temperature on the rate of polycondensation ( $\xi_0 = 0.04$ ). The binding of carbon dioxide by amino esters, in particular glycine ethyl ester, proceeds very vigorously—very rapidly and with evolution of heat.

In this reaction intermediate compounds of the type of carboxyamino esters are formed:



Compounds of this type were isolated and described by Frenkel and Katchalski [5]. They are unstable, and work with them therefore presents serious difficulties. It is probable that the true monomer in the polycondensation of an  $\alpha$ -amino ester is the carboxyamino ester. As the polycondensation proceeds (if it is carried out in a closed vessel), together with the formation of the reaction products—peptide esters and piperazinediones—by-products, such as alcohol, appear in the reaction mixture and carbon dioxide is regenerated. The regeneration of carbon dioxide ensures the formation of the carboxyamino ester. Hence, in the way in which it develops the

\* Communication 1: see [4].

develops, the polycondensation of  $\alpha$ -amino esters in presence of carbon dioxide is reminiscent of autocatalytic reactions.

With increase in the initial carbon dioxide concentration to  $\xi_0 = 0.16$  and higher, the rate of polycondensation increases; at the same time the average molecular weight of the resulting linear products falls and the monomer can be extracted from the viscous reaction mixture only with difficulty. In this case at the beginning of the reaction an intermediate product is formed, the nature of which has not yet been established. Frenkel and Katchalski [5] suggested that an intermediate carbamate compound  $R'OOC \cdot CHR \cdot NH_2 \cdot H \cdot OOC \cdot NH \cdot CHR \cdot COOR'$  may be formed. In an investigation of the reaction of  $\alpha$ -amino esters with anhydrides of carboxy amino acids, Bailly [6] isolated a thermolabile compound of this sort:



As the exact nature of the intermediaries in the polycondensation of  $\alpha$ -amino esters has not yet been established, the mechanism of the primary reaction, which determines the consumption of monomer, is unknown. Nevertheless, investigation of the temperature-dependence of the polycondensation kinetics indicates that the primary reaction of the monomer is associated with the formation of an intermediate thermolabile product and with its stability.

### EXPERIMENTAL

Measurement of the amount of free, unchanged glycine ethyl ester was carried out by the procedure described previously [4]. The reaction tube was opened, and its contents were transferred to a beaker, carefully rubbed out with absolute ether, filtered off, and washed several times on the filter until glycine ethyl ester had been removed completely. In order to prevent any condensation, the extract was cooled and treated immediately. A chromatographic check showed that the fresh ether extract contained only glycine ethyl ester, whereas this was absent in the solid residue remaining after the ether treatment. The chromatograms were prepared on

chromatographic paper No. 2 of the Leningrad No. 2 Paper Factory in the system butyl alcohol + acetic acid + water (4 : 1 : 5). Esters of glycine and peptides were detected by chlorination and coloration in a solution of o-toluidine and potassium iodide [7]. After removal of ether and ethanol from the ether extract in a vacuum, glycine ethyl ester was distilled off; the amount of the ester was determined gravimetrically. Figure 1 gives the experimental results obtained for various initial carbon dioxide concentrations:  $\xi_0 = 0.01, 0.02, 0.04, 0.08$ , and  $0.16$ . Examination of the experimental results showed that the primary reaction of binding glycine ethyl ester was of the first order for each given initial carbon dioxide concentration, for the kinetic relationship for the binding of monomer was represented by straight lines in a semi-logarithmic graph (Fig. 2). Hence, the first-order reaction found previously for  $\xi_0 = 0.02$  [4] is preserved also for other values of  $\xi_0$ . On the basis of these results, we calculated the values of the rate constants for the reaction of glycine ethyl ester in presence of various initial amounts of carbon dioxide (Table 1).

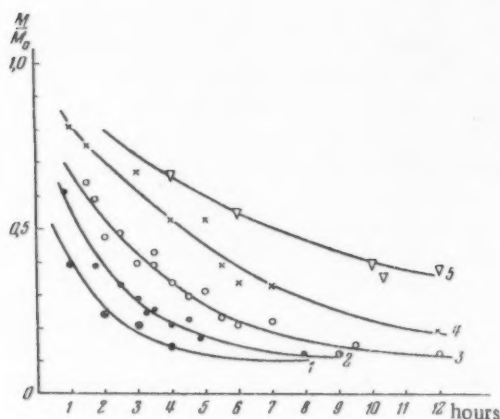


Fig. 1. Kinetics of removal of glycine ethyl ester by reaction: 1)  $\xi_0 0.16$ ; 2)  $\xi_0 0.08$ ; 3)  $\xi_0 0.04$ ; 4)  $\xi_0 0.02$ ; 5)  $\xi_0 0.01$ .

The quantitative data that we have obtained enable us to establish the character of the relationship between the rate constants for the reaction of glycine ethyl ester (at  $40^\circ$ ) and the initial carbon dioxide concentration. This relationship can be described by an expression of general form,  $k = A/\xi_0 + B$ , in which A and B are temperature-dependent constants. For  $40^\circ$  the relationship has the following form (Fig. 3):

$$k = 10^{-5} \left( 9.76 - \frac{0.0836}{\xi_0} \right) \text{sec}^{-1}.$$

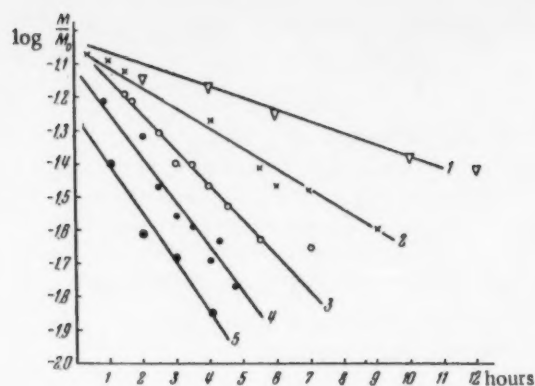


Fig. 2. Kinetics of removal of glycine ethyl ester by reaction: 1)  $\xi_0$  0.01; 2)  $\xi_0$  0.02; 3)  $\xi_0$  0.04; 4)  $\xi_0$  0.08; 5)  $\xi_0$  0.16.

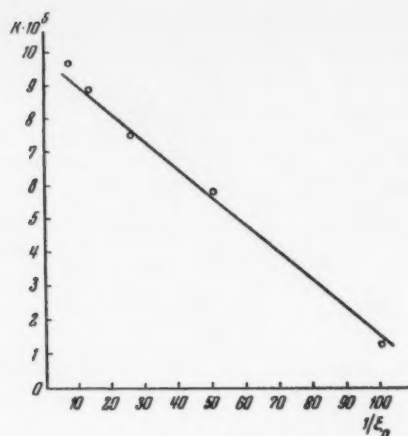


Fig. 3. Relation of rate constants for the binding of glycine ethyl ester ( $k$ ) to the initial carbon dioxide concentration  $\xi_0$  ( $40^\circ$ ).

By way of example we give data on the content of free monomer in the reaction mixture after four hours of reaction (Table 2). This time was chosen because even at high concentrations of carbon dioxide there is a fairly large amount of monomer and its concentration can be determined fairly accurately. At the same time, at low concentrations of carbon dioxide an appreciable amount of condensation products is formed in this time, and it is therefore possible to check the completeness of the extraction of glycine ethyl ester.

TABLE 1

Rate Constants for the Binding of Glycine Ethyl Ester  $k$  for Different Initial Carbon Dioxide Concentrations  $\xi_0$

$\xi_0$	$k \cdot 10^5$ (second $^{-1}$ ), experimental	$k \cdot 10^5$ (second $^{-1}$ ), theoretical
0.01	1.35	1.40
0.02	5.85	5.58
0.04	7.50	7.67
0.08	8.45	8.42
0.16	9.40	9.23

TABLE 2

Amount of Free Monomer ( $M$ ) in the Reaction Mixture for Different Carbon Dioxide Concentrations after 4 Hours of Reaction ( $40^\circ$ )

$\xi_0$	$M$ , theoretical	$M$ , experimental
0.01	0.816	0.776
0.02	0.448	0.526
0.04	0.332	0.340
0.06	0.300	0.243
0.08	0.286	0.256
0.16	0.265	0.235

Analogous calculations were carried out also for other times of reaction, and they also were in close accord with the experimental results. However, at times exceeding four hours very low values for  $\xi_0 = 0.08$  and 0.16 were obtained, for in the course of these periods the reaction mixture solidified and different kinetic laws are obeyed in the solid phase.

In our hypothesis, the stability of the hypothetical intermediate compound is of fundamental importance for the rate of consumption of monomer in the polycondensation of glycine ethyl ester. In this connection we carried out experiments on the measurements of the temperature dependence of the rate constants for the binding of glycine ethyl ester. The rate constants were calculated from the formula:

$$k_T = \frac{1}{\tau} \ln \frac{M(\tau)}{M_0}$$

In which  $M(\tau)$  is the amount of free monomer remaining unused at a time of  $\tau$  seconds after the start of reaction. Measurements were carried out in a thermostat controlled to within 0.01°;  $\xi_0 = 0.04$ , and  $\tau = 2$  and 4 hours.

The results are shown in Fig. 4.

From these data it was possible to calculate the activation energy of the primary process  $\Delta E_{1*} = 8.00$  kcal/mole (20° and above). A peculiar feature of the process is the reduction of the temperature coefficient of the rate constant of the reaction  $k_T + 10/k_T$  from 2.3 (in the range 0-20°) to 1.5 (20° and above). This probably indicates decomposition of the intermediate compound beginning at about 20°. The activation energy of the primary process below 20° is  $\Delta E_{1,2} = 13.8$  kcal/mole.

Hence, when the temperature rises above 20° the activation energy falls by  $\Delta E_{1,2} = 5.8$  kcal/mole.

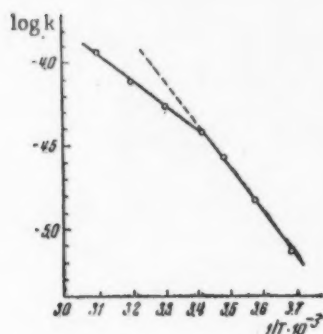


Fig. 4. Relation between rate constant  $k$  and temperature ( $\xi_0 = 0.04$ ).

#### SUMMARY

1. The kinetics of the binding of glycine ethyl ester in the course of its polycondensation were investigated. The relation between the rate constant of the reaction (first order) and the initial carbon dioxide concentration was determined over a range of carbon dioxide concentrations.

2. The temperature-dependence of the rate of binding of glycine ethyl ester was investigated.

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\* Original Russian pagination. See C. B. Translation.

# ORGANIC AND BIOLOGICAL CHEMISTRY

## ETHYLPHOSPHONOUS ESTERS AND SOME OF THEIR REACTIONS

### COMMUNICATION 7. MIXED ANHYDRIDES OF ETHYLPHOSPHONOUS ACID

#### AND DIALKYL HYDROGEN PHOSPHITES AND THE MIXED ANHYDRIDE OF

#### ETHYLPHOSPHONOUS ACID AND ISOPROPYL HYDROGEN ETHYLPHOS-

#### PHONITE. DIETHYL ETHYLPHOSPHONODITHIOITE

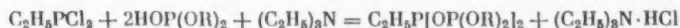
B. A. Arbuzov, N. I. Rizpolozhensky and M. A. Zvereva

The present communication is concerned with the synthesis of mixed anhydrides of ethylphosphonous acid and dialkyl hydrogen phosphites and the study of some of their properties.

We prepared the mixed anhydrides of ethylphosphonous acid and dialkyl hydrogen phosphites by the action of sodium dialkyl phosphite on ethylphosphonous dichloride (dichloroethylphosphine):



and by the action of dialkyl hydrogen phosphites on ethylphosphonous dichloride in presence of triethylamine in an ether medium:



The mixed anhydrides are colorless mobile liquids of unpleasant odor. They readily oxidize in the air. Cotton wool that has been moistened with one of these compounds rapidly begins to smolder. Constants of the compounds obtained are presented in the table.

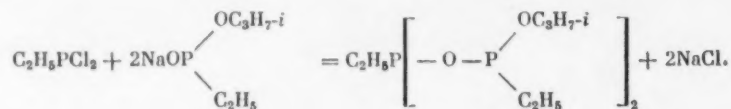
TABLE

No.	$\text{C}_2\text{H}_5\text{P[OP(OR)}_2\text{]}_2$	B. p. in °C (p in mm)	$n_D^{20}$	$d_4^{20}$	MR		Yield (%)
					Found	Calc.	
1	$\text{C}_2\text{H}_5\text{P[OP(OC}_2\text{H}_5\text{)}_2\text{]}_2$	126—128 (0.5)	1.4768	1.1524	82.82	83.36	48
2	$\text{C}_2\text{H}_5\text{P[OP(OC}_3\text{H}_7\text{-}n\text{)}_2\text{]}_2$	145—147 (1)	1.4662	1.0785	100.3	101.83	40
3	$\text{C}_2\text{H}_5\text{P[OP(OC}_3\text{H}_7\text{-}i\text{)}_2\text{]}_2$	130—132 (1)	1.4622	1.0693	100.4	101.83	51.5
4	$\text{C}_2\text{H}_5\text{P[OP(OC}_4\text{H}_9\text{-}i\text{)}_2\text{]}_2$	165—167 (2)	1.4643	1.0420	118.3	120.3	44.5

As in the case of the mixed anhydride of diethylphosphinous acid, we did not succeed in obtaining the methyl ester.



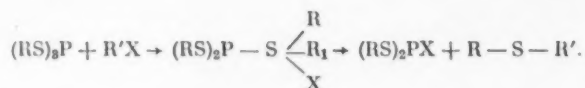
The mixed anhydride of ethylphosphonous acid and isopropyl hydrogen ethylphosphonite was prepared by the action of sodium isopropyl ethylphosphonite on ethylphosphonous dichloride:



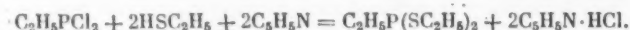
This anhydride is a liquid of unpleasant odor and readily oxidizes in the air: b.p. 144-146° (1 mm);  $n_D^{20}$  1.4928;  $d_4^{20}$  1.0778; Found MR 89.81; Calculated MR 90.71.

One of the most interesting reactions of mixed anhydrides of diethylphosphinous acid and dialkyl hydrogen phosphites consists in their conversion into quaternary phosphonium salts when treated with alkyl halides. A similar reaction occurs also in the case of the mixed anhydride of ethylphosphonous acid and diethyl hydrogen phosphite and will be considered in greater detail in our next communication. When it reacted with ethyl iodide (3 molecular proportions), tetraethylphosphonium iodide was obtained.

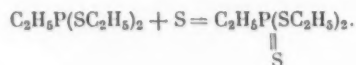
Divinsky, Kabachnik and Sidorenko [1], and also A. E. Arbuzov and Nikonov [2], showed that phosphorotriithious esters, when treated with alkyl halides and with acid chlorides, can undergo transformations not only of the type of the Arbuzov rearrangement, i.e., with addition and elimination at a phosphorus atom, but also with addition and elimination at a sulfur atom:



With the object of determining the course of reaction between alkyl halides and alkylphosphonodithious esters, we synthesized diethyl ethylphosphonodithioite:



This ester is a liquid of unpleasant odor. Unlike ethylphosphonous esters, it is not oxidized appreciably in the air. Its constants are: b.p. 98-100° (10 mm);  $n_D^{20}$  1.5490;  $d_4^{20}$  1.0200; Found MR 56.84; Calculated MR 56.52. It readily combines with sulfur with formation of diethyl ethylphosphonotrithioate, b.p. 91-93° (1 mm);  $n_D^{20}$  1.5861;  $d_4^{20}$  1.1300; Found MR 63.61; Calculated MR 62.74:

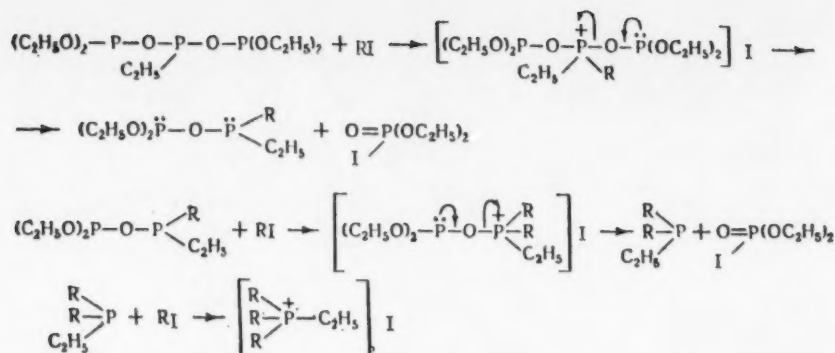


As a tervalent phosphorus derivative the ester reacts with cuprous iodide, but the reaction product could not be crystallized.

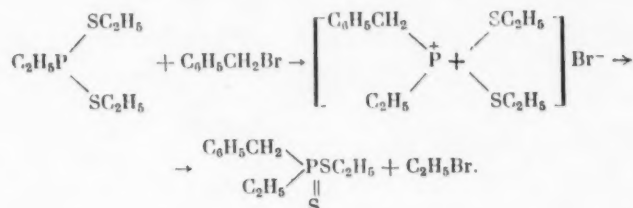
Interesting results were obtained by treating diethyl ethylphosphonodithioite with alkyl halides. Treatment with ethyl bromide gave triethylphosphine sulfide, m.p. 94-95°. Treatment with benzyl bromide gave two products: dibenzylethylphosphine sulfide, m.p. 127-127.5° and ethyl benzylethylphosphinodithioate, b.p. 136-138° (2 mm);  $n_D^{20}$  1.6070;  $d_4^{20}$  1.1272; Found MR 74.67; Calculated MR 73.82.

The formation of quaternary phosphonium salts by the action of alkyl halides on the mixed anhydride of ethylphosphonous acid and diethyl hydrogen phosphite can be explained as follows:

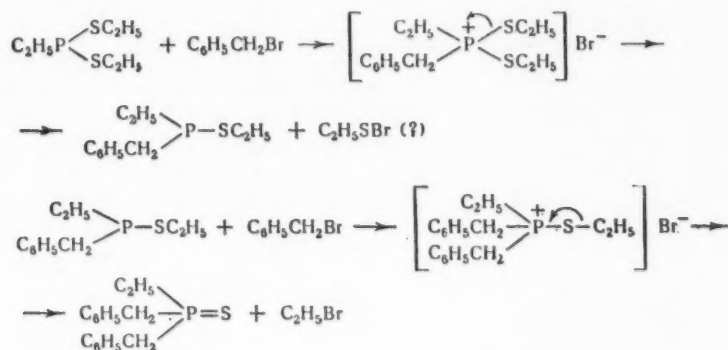




In the case of diethyl ethylphosphonodithioite, the experiments with benzyl bromide show that reaction can go in two directions. First there is the normal Arbuzov rearrangement:

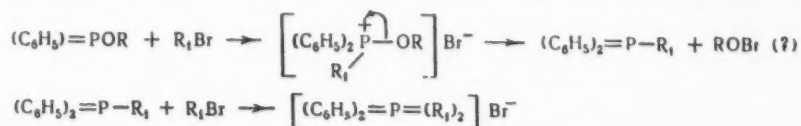


Second, together with the normal rearrangement, there evidently occurs the elimination of ethanesulfonyl bromide, which we did not succeed in trapping. This results in the formation of ethyl benzylethylphosphinothioite, which reacts with benzyl bromide with Arbuzov rearrangement and gives dibenzylethylphosphine sulfide:



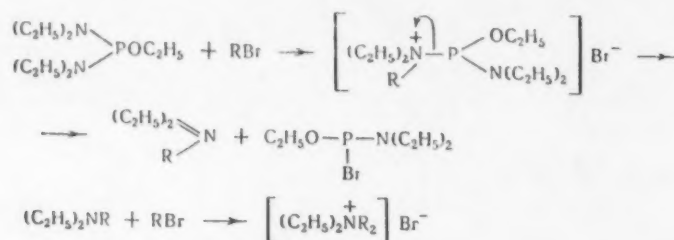
It is interesting to note that the formation of quaternary phosphonium salts was observed by A. E. Arbuzov in the case of diphenylphosphinothioic esters as early as 1914 [3].

Thus, treatment of ethyl diphenylphosphinothioite with ethyl iodide gave diethyldiphenylphosphonium iodide, and treatment with isobutyl iodide gave diisobutyldiphenylphosphonium iodide:



The formation of phosphonium salts in these cases can be explained on the basis of schemes analogous to those given above.

An analogous scheme may explain the formation of quaternary ammonium salts observed by Arbuzov and Yarmukhametova [4] in the reaction of alkyl halides with ethyl tetraethylphosphorodiamidite.



## EXPERIMENTAL

### 1. Synthesis of Mixed Anhydrides of Ethylphosphonous Acid and Dialkyl Hydrogen Phosphites and of the Mixed Anhydride of Ethylphosphonous Acid and Isopropyl Hydrogen Ethylphosphonite

1. Attempt to Synthesize the Mixed Anhydride of Ethylphosphonous Acid and Dimethyl Hydrogen Phosphite. A mixture of 150 ml of ether, 16.8 g of dimethyl hydrogen phosphite, and 15.5 g of triethylamine was prepared in a four-necked flask fitted with reflux condenser, dropping funnel, stirrer, and tube for the passage of carbon dioxide. The flask was cooled with snow and salt, and 10 g of ethylphosphonous dichloride was added to the vigorously stirred mixture. Stirring was then continued for two hours at room temperature. Triethylamine hydrochloride was filtered off at the pump in an atmosphere of carbon dioxide. Ether was distilled off, and the residue was vacuum-distilled from an Arbuzov flask. During distillation—at a bath temperature of 140°—the substance in the still decomposed with an explosion (before this happened, 3-4 g of material distilled over).

2. Synthesis of the Mixed Anhydride of Ethylphosphonous Acid and Diethyl Hydrogen Phosphite. a) Over a period of two hours, 40 g of ethylphosphonous dichloride was added to a cooled (snow and salt) ethereal solution of sodium diethyl phosphite prepared from 84.5 g of diethyl hydrogen phosphite and 15 g of sodium. The mixture was then stirred at the boiling point of ether in a water bath for two hours. The precipitate of sodium chloride was removed by centrifugation. The residue remaining after removal of ether was a colorless oily liquid of unpleasant odor. Vacuum distillation of the product was carried out on 15-20-g portions, since we found that with prolonged heating the substance decomposed with formation of low-boiling products, the composition of which we have not yet established. By vacuum distillation we isolated the mixed anhydride of ethylphosphonous acid and diethyl hydrogen phosphite, b.p. 126-128° (0.5 mm);  $d_4^{20}$  1.1524;  $n_D^{20}$  1.4768; Found MR 82.82; Calculated for  $\text{C}_{10}\text{H}_{25}\text{P}_3\text{O}_6$  MR 83.36. The yield of mixed anhydride was 49 g (48%).

Found %: P 27.95; 28.11  $\text{C}_{10}\text{H}_{25}\text{P}_3\text{O}_6$ . Calculated %: P 27.84

The mixed anhydride is a colorless oil having the unpleasant odor of phosphines; it is readily oxidized by atmospheric oxygen. Cotton wool moistened with the mixed anhydride begins to smoke and smolder after 1-2 minutes. For this reason, all operations in the synthesis of the mixed anhydride were carried out in an atmosphere of carbon dioxide.

b) A mixture of 300 ml of ether, 31.6 g of diethyl hydrogen phosphite, and 50 g of triethylamine was prepared in a four-necked flask fitted with reflux condenser, dropping funnel, stirrer, and tube for the passage of carbon dioxide. The flask was cooled with snow and salt, and 15 g of ethylphosphonous dichloride was added over a period of one hour. The reaction products were then stirred further at room temperature for two hours. Triethylamine hydrochloride was then filtered off under reduced pressure in a stream of carbon dioxide. Ether was distilled off leaving a colorless oily residue of unpleasant odor. The reaction product was distilled in

portions of about 15 g. Vacuum distillation from an Arbuzov flask gave the mixed anhydride of ethylphosphonous acid and diethyl hydrogen phosphite, b.p. 128-130° (1 mm);  $d_4^{20}$  1.1531;  $n_D^{20}$  1.4772; yield 19.2 g (51%).

Found %: P 27.62; 27.75  $C_{10}H_{25}P_3O_6$ . Calculated %: P 27.84

3. Synthesis of the Mixed Anhydride of Ethylphosphonous Acid and Dipropyl Hydrogen Phosphite. Over a period of one hour in a stream of carbon dioxide, 12.7 g of ethylphosphonous dichloride was added to an ethereal solution of sodium dipropyl phosphite prepared from 32 g of dipropyl hydrogen phosphite and 4.5 g of sodium. The mixture was stirred further for three hours at room temperature. The precipitate of sodium chloride was removed by centrifugation. Ether was distilled off under reduced pressure and left a colorless oily residue of unpleasant odor.

The reaction product was distilled in 15-17 g portions. Vacuum distillation from an Arbuzov flask gave the mixed anhydride of ethylphosphonous acid and dipropyl hydrogen phosphite, b.p. 145-148° (1 mm);  $d_4^{20}$  1.0785;  $n_D^{20}$  1.4662; Found MR 100.3; Calculated for  $C_{14}H_{33}P_3O_6$  MR 101.83. Yield 15.2 g (40%).

Found %: P 23.81; 23.95  $C_{14}H_{33}P_3O_6$ . Calculated %: P 23.84

The mixed anhydride of ethylphosphonous acid and dipropyl hydrogen phosphite is an oily liquid having an unpleasant phosphine odor. It is soluble in ether, benzene, and gasoline; it readily oxidizes in air. Cotton wool moistened with the mixed anhydride begins to smolder in 1-2 minutes.

4. Synthesis of the Mixed Anhydride of Ethylphosphonous Acid and Diisopropyl Hydrogen Phosphite. Over a period of one hour in a stream of carbon dioxide, 12.7 g of ethylphosphonous dichloride was added to an ethereal solution of sodium diisopropyl phosphite prepared from 32 g of diisopropyl hydrogen phosphite. Sodium chloride was removed by centrifugation. The residue remaining after removal of ether was a colorless oil having an unpleasant phosphine odor. As before, distillation was carried out in portions of 15-17 g. Vacuum distillation from an Arbuzov flask gave the mixed anhydride of ethylphosphonous acid and diisopropyl hydrogen phosphite, b.p. 130-132° (1 mm);  $d_4^{20}$  1.0693;  $n_D^{20}$  1.4622; Found MR 100.4; Calculated for  $C_{14}H_{33}P_3O_6$  MR 101.83.

Found %: P 23.5; 23.63  $C_{14}H_{33}P_3O_6$ . Calculated %: P 23.84

The mixed anhydride readily oxidized in the air.

5. Synthesis of the Mixed Anhydride of Ethylphosphonous Acid and Diisobutyl Hydrogen Phosphite. A mixture of 200 ml of ether, 23.8 g of diisobutyl hydrogen phosphite, and 10 g of pyridine was prepared in a four-necked flask. The mixture was stirred and cooled with snow and salt, and 8 g of ethylphosphonous dichloride was added over a period of 40 minutes. The reaction product was then stirred further for two hours at room temperature. Pyridine hydrochloride was filtered off at the pump in a stream of carbon dioxide. The residue remaining after removal of ether was a slightly yellowish oil of unpleasant odor. Vacuum distillation from an Arbuzov flask gave the mixed anhydride, b.p. 165-167° (2 mm);  $d_4^{20}$  1.0420;  $n_D^{20}$  1.4643; Found MR 118.3; Calculated MR for  $C_{18}H_{41}P_3O_6$  120.3; yield 12 g (44.5%).

Found %: P 21.12; 21.23  $C_{18}H_{41}P_3O_6$ . Calculated %: P 20.84

The mixed anhydride is a colorless oil having an unpleasant phosphine odor. It readily oxidizes in the air; cotton wool moistened with the mixed anhydride begins to smolder after 1-2 minutes.

6. Synthesis of the Mixed Anhydride of Ethylphosphonous Acid and Isopropyl Hydrogen Ethylphosphonite. The procedure was similar to that described above. The reactants were isopropyl hydrogen ethylphosphonite (16 g), ethylphosphonous dichloride (9.3 g), and triethylamine (18.5 g). Vacuum distillation of the product gave the mixed anhydride, b.p. 144-146° (1 mm);  $d_4^{20}$  1.0778;  $n_D^{20}$  1.4928; Found MR 89.81; Calculated for  $C_{12}H_{29}P_3O_4$  MR 90.71:

Found %: P 28.33; 28.20  $C_{12}H_{29}P_3O_4$ . Calculated %: P 28.13

The mixed anhydride readily oxidized in the air. It is soluble in ether, gasoline and benzene. It has an unpleasant odor.

7. Action of Ethyl Iodide on the Mixed Anhydride of Ethylphosphonous Acid and Diethyl Hydrogen Phosphate. A mixture of 6 g of the mixed anhydride and 8.5 g of ethyl iodide was prepared in a three-necked flask fitted with reflux condenser, thermometer, and tube for passage of carbon dioxide. No reaction occurred at room temperature. When the mixture was heated to 138-140°, reaction set in and the temperature in the flask began to rise rapidly in spite of the fact that heat was no longer being applied. Toward the end of the reaction, the temperature in the flask attained 220°. The contents of the flask solidified. Crystallization from isopropyl alcohol gave needles melting with decomposition at 270-276°.

Found %: P 11.62; 11.53; I 46.17; 46.21  $C_8H_{20}PI$  Calculated %: P 11.31; I 46.4

The product was therefore tetraethylphosphonium iodide.

## II. Synthesis and Reactions of Diethyl Ethylphosphonodithioite

1. Synthesis of Diethyl Ethylphosphonodithioite. A mixture of 45.6 g of ethanethiol, 58 g of pyridine, and 300 ml of ether was prepared in a three-necked flask fitted with reflux condenser, dropping funnel, and stirrer. The mixture was cooled with snow and salt and was stirred while 48.1 g of ethylphosphonous dichloride was added over a period of 90 minutes. Stirring of the reaction products continued further for three hours at room temperature. Pyridine hydrochloride was filtered off at the pump. The residue (69 g) after removal of ether was vacuum-fractionated from an Arbuzov flask and gave 50 g (74%) of diethyl ethylphosphonodithioite, b.p. 98-100° (10 mm);  $d_4^{20}$  1.0200;  $n_D^{20}$  1.5490; Found MR 56.84; Calculated for  $C_6H_{15}PS_2$  MR 56.52:

Found %: P 17.1; 17.21; S 35.32; 35.25  $C_6H_{15}PS_2$ . Calculated %: P 17.0; S 35.2

Diethyl ethylphosphonodithioite is a colorless mobile liquid having a specific, unpleasant odor. It is insoluble in water, but soluble in ether, gasoline, benzene, and alcohol. Unlike its oxygen analogs, it does not oxidize appreciably in the air.

2. Action of Sulfur on Diethyl Ethylphosphonodithioite. A mixture of 6.8 g of the ester and 1.2 g of sulfur powder was prepared in a three-necked flask fitted with reflux condenser and thermometer. There was no reaction in the cold, but on heating to 100° the reaction of addition of sulfur set in. In spite of the fact that the application of heat was stopped, the temperature in the flask rose rapidly and attained 185° toward the end of the reaction. The contents of the flask became deep brown. All of the sulfur reacted. Vacuum distillation from an Arbuzov flask gave diethyl ethylphosphonotrithioate, b.p. 91-93° (1 mm);  $d_4^{20}$  1.1300;  $n_D^{20}$  1.5861; Found MR 63.61; Calculated for  $C_6H_{15}PS_3$  MR 62.74.

Found %: P 14.53; 14.40; S 44.68; 44.75  $C_6H_{15}PS_3$ . Calculated %: P 14.49; S 44.8

3. Action of Cuprous Iodide on Diethyl Ethylphosphonodithioite. The ester (2 g) was mixed with cuprous iodide (2.4 g) in a test tube fitted with a thermometer. The temperature rose from 20° to 55°, but not all of the cuprous iodide dissolved and it was necessary to apply heat. On heating to 160° almost the whole of the cuprous salt dissolved. A very viscous yellow sirup was obtained, and we did not succeed in crystallizing it.

4. Action of Benzyl Bromide on Diethyl Ethylphosphonodithioite. A mixture of 5 g of the ester and 4.7 g of benzyl bromide was prepared in a three-necked flask fitted with reflux condenser and thermometer. There was no reaction in the cold, but on heating to 140° reaction set in. The temperature in the flask began to rise rapidly and attained 180° toward the end of the reaction, in spite of the fact that external heating was discontinued. When the flask was cooled, fine needles began to be precipitated. After two days the contents of the flask were diluted with petroleum ether and filtered. The crystals were recrystallized from isopropyl alcohol when they melted at 127-127.5°.

Found %: C 70.25; 70.11; H 7.32; 7.12; P 11.42; 11.55; S 11.62; 11.75  $C_{16}H_{19}PS$ . Calculated %: C 70.02; H 6.94; P 11.32; S 11.68

The analysis and melting point confirmed that the product was dibenzylethylphosphine sulfide.

After removal of ether, the filtrate was vacuum-fractionated from an Arbuzov flask. The product isolated had b.p. 136-138° (2 mm);  $d_4^{20}$  1.1272;  $n_D^{20}$  1.6070; Found MR 74.67; Calculated for  $C_{11}H_{17}PS_2$  MR 73.82.

Found %: P 12.68; 12.75; S 26.36; 26.42  $C_{11}H_{17}PS_2$ . Calculated %: P 12.72; S 26.21

Hence, as confirmed by analysis, the second reaction product was ethyl benzylethylphosphinodithioate.

5. Action of Ethyl Bromide on Diethyl Ethylphosphonodithioite. The reaction was carried out in sealed glass tubes. Reaction was between 11.5 g of the ester and 7 g of ethyl bromide. The tube was heated in oil at 140-150° for nine hours. When the tube was cooled, needle-like crystals separated. When the tube was opened it was found that there was no excess pressure. The crystals were filtered off at the pump and recrystallized from isopropyl alcohol. Recrystallization gave needles of m.p. 94-95°.

Found %: P 20.42; 20.36; S 21.1; 21.38  $C_8H_{15}PS$ . Calculated %: P 20.65; S 21.32

Hence, as confirmed by the analysis and melting point, the crystalline reaction product was triethylphosphine sulfide. We have not yet succeeded in establishing the compositions and structures of the liquid reaction products.

#### SUMMARY

1. Mixed anhydrides of ethylphosphonous acid and dialkyl hydrogen phosphites were prepared.
2. It was shown that treatment of the mixed anhydrides with alkyl halides resulted in rearrangement with formation of quaternary phosphonium salts.
3. Diethyl ethylphosphonodithioite was prepared.
4. Diethylethylphosphonotrithioate was obtained by addition of sulfur to diethyl ethylphosphonodithioite.
5. It was found that treatment of diethyl ethylphosphonodithioite with benzyl bromide results in the formation of dibenzylethylphosphine sulfide and ethyl benzylethylphosphinodithioate.

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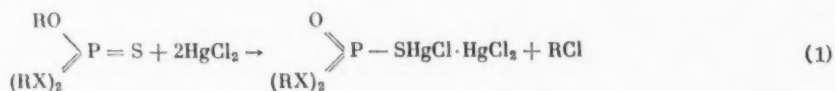
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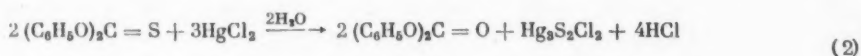
# REACTION OF MERCURIC ACETATE WITH XANTHIC ESTERS

R. Kh. Freidlina and E. Ts. Chukovskaya

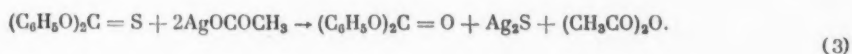
Various organic compounds containing thione sulfur— of the type  $(RO)_{n-2}E=S$ , in which E is an  $n$ -valent element— are not inert to the action of mercury salts. As Pishchimuka found [1], when mercuric chloride is heated with phosphorothionic esters, these thione compounds are converted into thiol compounds:



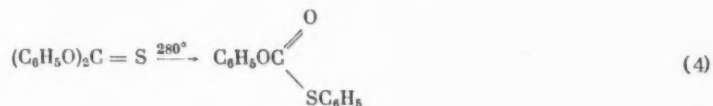
Thionocarbonic esters react with mercuric chloride in a different way [2]. Thus, reaction between O,O-diphenyl thiocarbonate and mercuric chloride occurs only in presence of water and then gives diphenyl carbonate and a mercury salt of composition  $Hg_3S_2Cl_2$ :



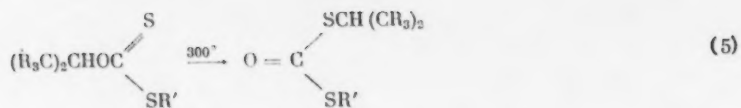
When O,O-diphenyl thiocarbonate reacts with salts of heavy metals and carboxylic acids, the process takes the same course even in absence of water:



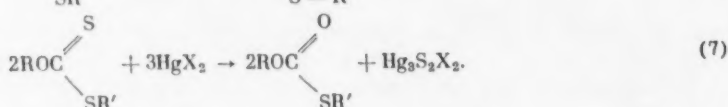
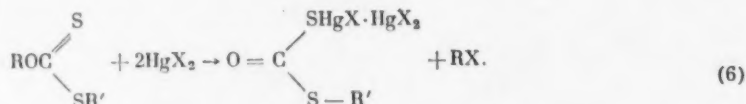
In the reaction of thionocarbonic esters with heavy-metal salts no isomerization products analogous to those obtained in the Pishchimuka reaction are formed. It is interesting that, when heated, thionocarbonic esters can undergo isomerization into thiolcarbonic esters [3]:



The action of mercury salts on xanthic esters has not been described. Under the action of heat, xanthic esters of the type  $(R_3C)_2CHOCS_2R$  (which are unable to undergo Chugaev breakdown with formation of unsaturated hydrocarbons with the skeleton of the O-alkyl of the original ester) undergo isomerization with formation of dithiolcarbonic esters [4]:



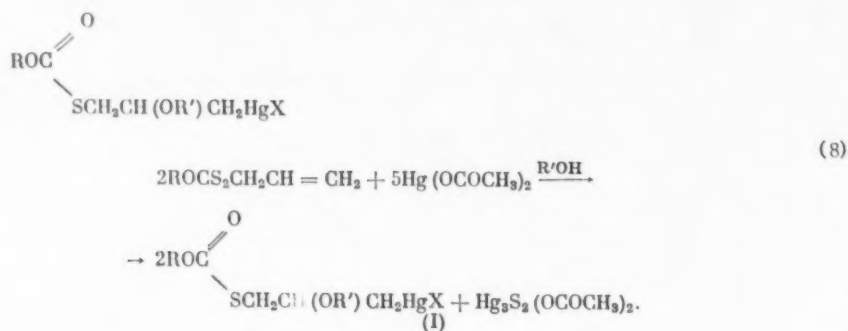
On analogy with the above-described reactions, it might be expected that mercuric salts would react with alkylxanthic esters in accordance with scheme (6) or (7):



Our investigation shows that reaction between alkylxanthic esters and mercuric acetate proceeds already at room temperature in both of the directions indicated.

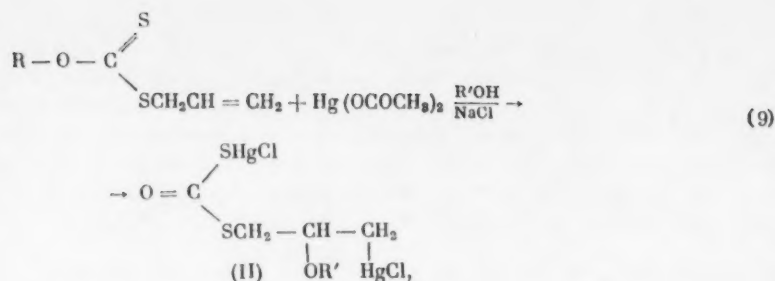
Preliminary experiments showed that, in order to obtain stable products it is necessary to use two molecular proportions of mercuric salt to one of xanthic ester: when equimolecular amounts of reactants are used there separates a white, rapidly blackening precipitate, which we have not investigated further. In the reaction between mercuric acetate and methyl methylxanthate we obtained an amorphous insoluble precipitate corresponding in composition to  $\text{Hg}_3\text{S}_2(\text{OCOCH}_3)_2$ . By addition of sodium chloride to the filtrate another insoluble mercury-containing compound was obtained, but owing to purification difficulties it was not investigated further. We then studied the action of mercuric acetate on allyl methylxanthate and allyl hexylxanthate in media of methyl, ethyl and propyl alcohols at room temperature. Allyl esters were chosen for investigation on the assumption that the reaction products would be readily isolated as individual compounds in the form of their adducts with mercuric acetate formed by addition at the allyl double bond.

In all cases studied the principal direction of reaction was the formation of an insoluble infusible amorphous solid of composition  $\text{Hg}_3\text{S}_2(\text{OCOCH}_3)_2$  and of readily soluble low-melting compounds of structure:



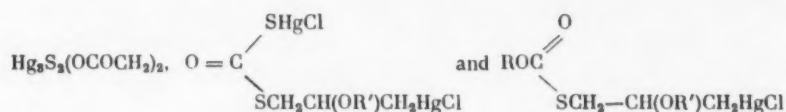
in which  $\text{R} = \text{CH}_3, n\text{-C}_6\text{H}_{13}$ ;  $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7$ .

Reactions with isomerization according to Scheme (9), analogous to the Pishchimuka reaction, occurred with considerably lower yields of products:



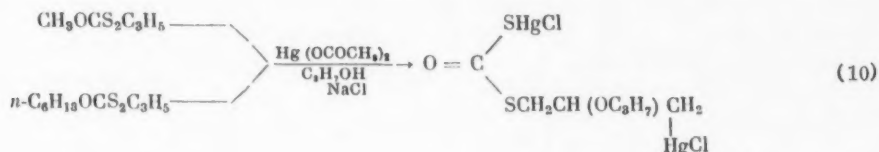
in which  $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7$ ;  $\text{R} = \text{CH}_3, n\text{-C}_6\text{H}_{13}$ .

The bischloromercuri derivatives of Structure (II) are much less soluble than compounds of Structure (I). The considerable differences in solubility between the three mercury-containing compounds formed in the reaction

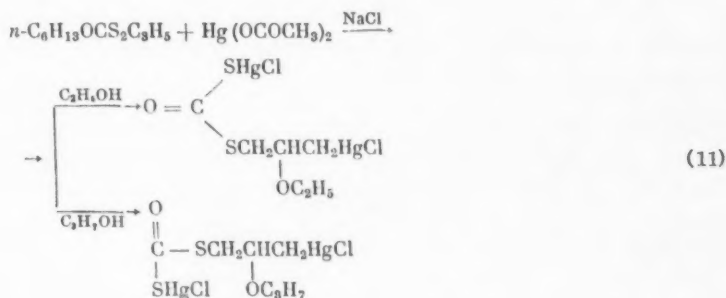


made it possible for them to be isolated and for the transformations under consideration to be studied in fair detail.

When the reactions between mercuric acetate and the allyl esters of methyl- and hexyl-xanthic acids were carried out in propyl alcohol, apart from the compounds formed in accordance with Scheme (8), in both cases the same compound  $\text{C}_7\text{H}_{12}\text{S}_2\text{O}_2\text{Hg}_2\text{Cl}_2$  was formed, which shows that reaction proceeded with elimination of the O-allyl in accordance with Scheme (10):



When reaction between mercuric acetate and allyl hexylxanthate was carried out in media of ethyl and propyl alcohols, apart from compounds formed in accordance with Scheme (8), two different products  $\text{C}_6\text{H}_{10}\text{O}_2\text{S}_2\text{Hg}_2\text{Cl}_2$  and  $\text{C}_7\text{H}_{12}\text{O}_2\text{S}_2\text{Hg}_2\text{Cl}_2$ , respectively, were obtained, which proves the participation of the medium in these reactions (Scheme 11), as in all cases studied of addition of mercuric acetate to olefins:



## EXPERIMENTAL

**1. Allyl Methylxanthate.** Potassium methylxanthate (90 g, i.e., 0.61 mole) was dissolved by heating it with methanol (300 ml). The solution was cooled to room temperature, and with vigorous mechanical stirring 50 g (0.65 mole) of allyl chloride was added. The reaction mixture was boiled for six hours, cooled, and diluted with water. The oil that formed was separated, and the aqueous layer was extracted with ether. The oil and ether extracts were dried over calcium chloride, ether was distilled off, and the residue was vacuum-fractionated. A second distillation gave 56 g (63%) of product, b.p. 79° (8 mm);  $n_D^{20}$  1.5620;  $d_4^{20}$  1.1313; Found MR 43.43; Calculated for  $C_5H_8S_2O$  MR 42.95.

Found %: C 40.94; 40.82; H 5.28; 5.08; S 42.93; 42.84. Calculated %: C 40.54; H 5.40; S 43.24

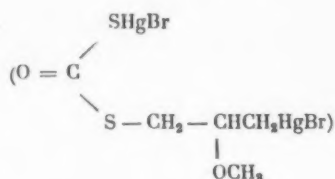
**2. Allyl Hexylxanthate.** The same procedure was used. From 285 g (5 moles) of potassium hydroxide, 650 ml (6.3 moles) of hexyl alcohol, and 380 g (5 moles) of carbon disulfide, 250 g of potassium hexylxanthate was prepared. Treatment of 165 g (0.7 mole) of the crude salt with 70 g (0.9 mole) of allyl chloride in 700 ml of methanol gave (two vacuum distillations) 68 g (41%) of allyl hexylxanthate, b.p. 120-122° (2 mm);  $n_D^{20}$  1.5230;  $d_4^{20}$  1.0157; Found MR 65.68; Calculated for  $C_{10}H_{18}S_2O$  MR 65.91.

**3. Methyl Methylxanthate.** This was prepared in 61% yield; b.p. 86° (54 mm);  $n_D^{20}$  1.5665;  $d_4^{20}$  1.1765; Found MR 33.92; Calculated for  $C_3H_6S_2O$  MR 34.05. The literature [5] gives:  $n_D^{16}$  1.5704;  $d_4^{20}$  1.176.

**4. Action of Mercuric Acetate on Allyl Methylxanthate.** a) **In Methyl Alcohol.** A solution of 4.5 g (0.03 mole) of allyl methylxanthate in 50 ml of methyl alcohol was added at room temperature to a solution of 28.6 g (0.09 mole) of mercuric acetate in 400 ml of methyl alcohol. An amorphous white precipitate formed. The precipitate was filtered off, washed and dried in the air; weight 9 g (77% yield). It was a white substance, insoluble in the usual organic solvents; it decomposed without melting.

Found %: C 6.30; 6.42; H 0.93; 0.92  $Hg_3S_2C_4O_4H_6$ . Calculated %: C 6.11; H 0.76

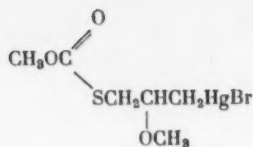
The filtrate obtained after separation of the amorphous precipitate was treated with saturated aqueous potassium bromide solution until precipitation was complete. The precipitate was filtered off; weight 3.7 g (17% yield). It dissolved when heated with a large excess of water, alcohol, or ethyl acetate. It decomposed at above 110° without melting. With potassium hydroxide in the cold it gave a precipitate of mercuric oxide. This substance



was recrystallized from ethyl alcohol.

Found %: C 8.21; 8.09; H 1.48; 1.49; Br 22.59; 22.44  $C_5H_8S_2O_2Hg_2Br_2$ . Calculated %: C 8.27; H 1.10; Br 22.10

The filtrate was evaporated at the water pump down to a volume of 30-40 ml. Separation into layers occurred. The lower layer, which consisted of a thick yellow oil, was separated; after standing for a short time it crystallized; weight 8 g (60.2% yield). Two recrystallizations from ethyl alcohol gave glistening white crystals of



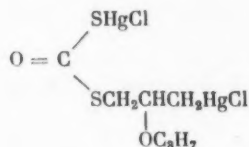
m.p. 59-60°.

Found %: C 16.30; 16.18; H 2.59; 2.46; Br 18.06; 18.24  $\text{C}_6\text{H}_{11}\text{O}_3\text{SHgBr}$ . Calculated %: C 16.25; H 2.48; Br 18.06

When the filtrate obtained after separation of the precipitate of  $\text{Hg}_3\text{S}_2(\text{OCOCH}_3)_2$  was treated with sodium chloride, instead of potassium bromide as described above, a chloride was precipitated which we did not succeed in obtaining in a pure form. From the filtrate obtained after its separation we isolated S-3-(chloromercuri)-2-methoxypropyl O-methyl thiolcarbonate in 65% yield (by the procedure described above for the bromo compound); white glistening crystals, m.p. 65-66° (from ethyl alcohol).

Found %: C 18.33; 18.21; H 2.68; 2.68; Cl 8.80; 9.06  $\text{C}_6\text{H}_{11}\text{O}_3\text{SHgCl}$ . Calculated %: C 18.04; H 2.75; Cl 8.79

b) In Propyl Alcohol. The above-described procedure was applied to 10 g (0.067 mole) of allyl methylxanthate and 44 g (0.134 mole) of mercuric acetate dissolved in 1 liter of propyl alcohol acidified with acetic acid. After separating the precipitate of  $\text{Hg}_3\text{S}_2(\text{OCOCH}_3)_2$  and adding sodium chloride solution, we obtained 5.2 g (11%) of S-chloromercuri S-3-(chloromercuri)-2-propoxypropyl dithiolcarbonate:



The substance was recrystallized from ethyl alcohol.

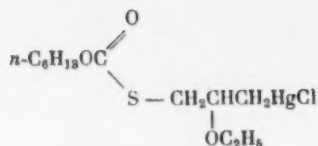
Found %: C 12.20; 12.14; H 1.82; 1.76; Cl 10.18; 10.30  $\text{C}_7\text{H}_{12}\text{S}_2\text{O}_2\text{Hg}_2\text{Cl}_2$ . Calculated %: C 12.65; H 1.80; Cl 10.69

5. Action of Mercuric Acetate on Allyl Hexylxanthate. a) In Ethyl Alcohol. Allyl hexylxanthate (4.3 g, i.e., 0.02 mole) was added to a solution of 19.0 g (0.06 mole) of mercuric acetate in 300 ml of ethyl alcohol acidified with acetic acid. After separation of the precipitate of  $\text{Hg}_3\text{S}_2(\text{OCOCH}_3)_2$  (6.3 g, i.e., 80% yield), the filtrate was treated with saturated brine. The resulting precipitate (1.8 g, i.e., 14.5% yield) was purified by recrystallization from alcohol. It was assigned the structure:



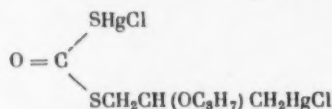
Found %: C 10.75; 10.86; H 1.78; 1.82; Cl 11.14; 10.93  $\text{C}_6\text{H}_{10}\text{S}_2\text{Cl}_2\text{O}_2\text{Hg}_2$ . Calculated %: C 11.00; H 1.53; Cl 10.85

The filtrate was evaporated at the pump down to a volume of 30-40 ml. Separation into layers occurred. The lower layer, a thick colorless oil (6.8 g, i.e., 70.3% yield) was separated and purified by repeated freezing out of alcohol. The substance was again obtained as an oil. It was vacuum-dried. It was assigned the structure:



Found %: C 29.62; 29.48; H 4.74; 4.80; Cl 7.38; 7.40  $\text{C}_{13}\text{H}_{23}\text{SO}_3\text{HgCl}$ . Calculated %: C 29.81; H 4.76; Cl 7.22

b) In Propyl Alcohol. The same procedure was applied to 18 g (0.082 mole) of allyl hexylxanthate and 53 g (0.16 mole) of mercuric acetate dissolved in 1 liter of propyl alcohol acidified with acetic acid. We obtained 7.5 g (15%) of S-chloromercuri S-3-(chloromercuri)-2-propoxypropyl dithiolcarbonate:



The substance was recrystallized from ethyl alcohol.

Found %: C 29.62; 12.93; H 2.04; 1.93; Cl 10.78; 10.66  $\text{C}_7\text{H}_{12}\text{Hg}_2\text{Cl}_2\text{O}_2\text{S}_2$ . Calculated %: C 12.65; H 1.80; Cl 10.69

6. Action of Mercuric Acetate on Methyl Methylxanthate. From a solution of 3.6 g (0.03 mole) of methyl methylxanthate and 19.0 g (0.06 mole) of mercuric acetate in 300 ml of methyl alcohol, 9 g (76%) of an amorphous powder  $\text{Hg}_3\text{S}_2(\text{OCOCH}_3)_2$  was obtained.

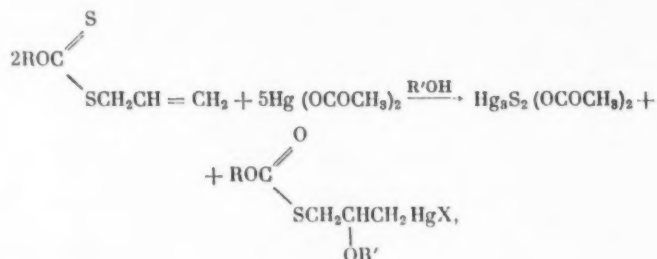
Found %: C 6.20, 6.37; H 0.96, 1.11  $\text{Hg}_3\text{S}_2\text{C}_4\text{O}_4\text{H}_6$ . Calculated %: C 6.11; H 0.76

A substance (1.8 g) was obtained from the filtrate by addition of brine. It was a white amorphous powder, infusible and insoluble in the usual organic solvents. It could not be purified by washing.

#### SUMMARY

1. A study was made of the reaction of mercuric acetate with allyl esters of methyl- and hexyl-xanthic acids and with methyl methylxanthate in media of methyl, ethyl, and propyl alcohols.

2. It was shown that reaction is mainly in the direction of the formation of mercury derivatives of thiol-carbonic acid, thione sulfur being replaced by oxygen in accordance with the scheme:

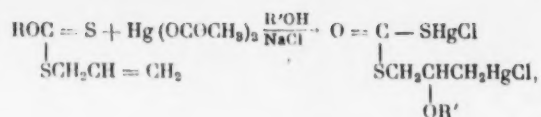


in which  $\text{R} = \text{CH}_3$ ,  $n\text{-C}_6\text{H}_{13}$ ;  $\text{R}' = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ .

3. It was shown that with xanthic esters reaction occurs with conversion of a thione derivative into a thiol derivative, which is analogous to the reaction with phosphorothionic esters described by Pishchimuka. The



reaction scheme is:



in which R = CH<sub>3</sub>, n-C<sub>6</sub>H<sub>13</sub>; R' = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub>.

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## 2-CHLOROETHYL ESTERS OF SOME PHOSPHORUS ACIDS

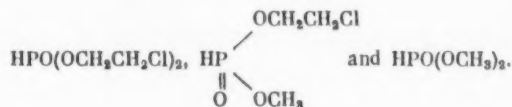
E. L. Gefter and M. I. Kabachnik

In a series of papers by one of us and Rossiiskaya the preparation and some reactions of 2-chloroethyl esters of alkyl and aryl dihydrogen phosphites [1-4], of 2-chloroethylphosphonic acid [2], and of vinylphosphonic acid [5] were described. As we considered it desirable to extend the range of known substances of this type, we synthesized some symmetrical and mixed 2-chloroethyl esters of phosphorous, phosphoric, and certain phosphonic acids, most of which have not been described previously.

Representatives of the first group of substances were prepared by reaction of phosphorus trichloride with 2-chloroethanol, alone or mixed with methanol. From phosphorus trichloride and 2-chloroethanol we obtained bis-2-chloroethyl hydrogen phosphite in 63% yield:



It will be obvious that it is impossible to synthesize the mixed 2-chloroethyl methyl hydrogen phosphite in good yield by the action of a mixture of the two alcohols on phosphorus trichloride, since all three possible dialkyl hydrogen phosphites are bound to be obtained in this reaction:

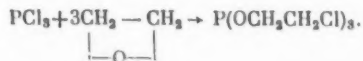


When the reaction is carried out at temperatures ranging from 0° to 20-22°, it is in fact found that all three dialkyl hydrogen phosphites are formed, the mixed ester being obtained in 18-19% yield.

Among derivatives of phosphoric acid we obtained 2-chloroethyl diethyl phosphate in good yield from diethyl phosphorochloridate and 2-chloroethanol in presence of pyridine:

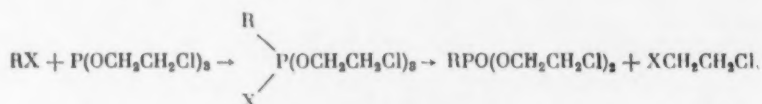


In the synthesis of bis-2-chloroethyl alkylphosphonates we started from tris-2-chloroethyl phosphite, which was prepared by Kabachnik and Rossiiskaya's method [1] from phosphorus trichloride and ethylene oxide:



The Arbuzov rearrangement of tris-2-chloroethyl phosphite has received very little study. Kabachnik and Rossiiskaya [2] showed that thermal treatment of tris-2-chloroethyl phosphite resulted in its isomerization to bis-2-

chloroethylphosphonate, the part of the alkyl halide rearrangement agent being played by the alkyl halide function of the phosphorous ester itself. Also, Efimova [6] carried out the reaction of tris-2-chloroethyl phosphite with 1,2-dichloroethane and three different alkyl bromomethyl ethers and obtained, correspondingly, bis-2-chloroethyl esters of 2-chloroethylphosphonic acid. In the reaction of tris-2-chloroethyl phosphite with alkyl halides, two competing processes are possible: the above-mentioned isomerization and the usual Arbuzov reaction between a phosphorous ester and an alkyl halide



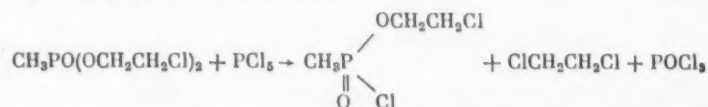
As the isomerization of tris-2-chloroethyl phosphite is observed at 150–160°, the occurrence of one or another possible reaction (or of both simultaneously) is evidently determined by the temperature at which the process is carried out. We investigated the action of methyl and ethyl iodides and acetyl chloride on tris-2-chloroethyl phosphite, the components being heated together in the molar ratio of 1:1–1.2. When a certain temperature was attained in the reaction mixture, an exothermic reaction of short duration occurred. The mixture was then heated for a further short time, after which dichloro- or chloriodo-ethane was distilled off and the residue was vacuum-distilled. The yields of bis-2-chloroethyl esters obtained were: 85% of methylphosphonic ester, 75% of ethylphosphonic ester, and 50% of acetylphosphonic ester. In every case, particularly the last, a nondistilling residue remained which was not investigated further. The nature of residues of this sort was considered in the above-mentioned paper [2].

TABLE

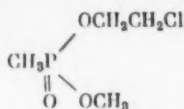
No.	Formula of substance	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	MR		Yield (%)
					Found	Calc.	
1	$\text{HPO}(\text{OCH}_2\text{CH}_2\text{Cl})_2^*$	119–120 (3.5–4)	1.4025	1.4708	41.25	41.27	63
2	$\begin{array}{c} \text{HP} \\ \diagup \quad \diagdown \\ \text{OCH}_2\text{CH}_2\text{Cl} \quad \text{OCH}_3 \\ \parallel \\ \text{O} \end{array}$	85–87 (3)	1.3162	1.4417	31.86	31.79	19
3	$(\text{C}_2\text{H}_5\text{O})_2\text{POCH}_2\text{CH}_2\text{Cl}^*$	95–97 (1–1.5)	1.1949	1.4279	46.64	46.76	72.5
4	$\begin{array}{c} \text{CH}_3\text{PO}(\text{OCH}_2\text{CH}_2\text{Cl})_2 \\ \parallel \\ \text{O} \end{array}$	124–125 (3)	1.3437	1.4671	45.66	45.89	85
5	$\text{C}_2\text{H}_5\text{PO}(\text{OCH}_2\text{CH}_2\text{Cl})_2$	124–125 (2.5)	1.3151	1.4700	49.9	50.5	70.5
6	$\begin{array}{c} \text{CH}_3\text{COPO}(\text{OCH}_2\text{CH}_2\text{Cl})_2 \\ \parallel \\ \text{O} \end{array}$	138–139 (3–4)	1.3729	1.4726	50.77	50.52	52
7	$\begin{array}{c} \text{CH}_3\text{P} \\ \diagup \quad \diagdown \\ \text{OCH}_2\text{CH}_2\text{Cl} \quad \text{Cl} \\ \parallel \\ \text{O} \end{array}$	92–93 (5)	1.3862	1.4658	35.30	35.38	50.5
8	$\begin{array}{c} \text{CH}_3\text{P} \\ \diagup \quad \diagdown \\ \text{OCH}_2\text{CH}_2\text{C} \quad \text{OCH}_3 \\ \parallel \\ \text{O} \end{array}$	86–88 (1)	1.2680	1.4448	36.21	36.40	39

\* Only boiling points are given in the literature [7, 8].

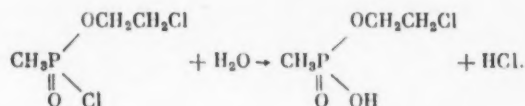
By careful treatment of bis-2-chloroethyl methylphosphonate with phosphorus pentachloride we succeeded in isolating 2-chloroethyl methylphosphonochloridate:



(together with some methylphosphonic dichloride). By treating this phosphonochloridate with methanol we obtained the mixed 2-chloroethyl methyl ester of methylphosphonic acid:



and by the action of water we obtained the corresponding acid ester:



The constants and yields of the products are given in the table.

#### EXPERIMENTAL

**Bis-2-chloroethyl Hydrogen Phosphite.** Phosphorus trichloride (69 g) was added with stirring over a period of two hours to 2-chloroethanol (121 g) at 15–25°, and stirring was continued for one hour. Distillation at 3.5 to 4 mm gave Fraction I, 4.8 g, b.p. 41–110°; Fraction II, 9 g, b.p. 110–119°; Fraction III, 66 g (63% yield) of bis-2-chloroethyl hydrogen phosphite, b.p. 119–120°. For constants see table, No. 1.

Found %: P 14.82; C 23.16, 23.01; H 4.44, 4.34.  $\text{C}_4\text{H}_9\text{O}_3\text{Cl}_2\text{P}$ . Calculated %: P 14.98; C 23.20; H 4.38

Bis-2-chloroethyl hydrogen phosphite is a clear colorless liquid of sharp unpleasant odor, soluble in alcohol, ether, benzene and toluene, but insoluble in water.

**2-Chloroethyl Methyl Hydrogen Phosphite.** Phosphorus trichloride (68.7 g) was added at 19.25° to a mixture of methanol (16 g) and 2-chloroethanol (80.5 g). The reaction time was three hours with a period of further stirring of 30 minutes. Distillation at 3 mm gave four fractions, of which the first and the fourth consisted of somewhat contaminated dimethyl and bis-2-chloroethyl hydrogen phosphites, respectively. Redistillation of the second fraction gave pure 2-chloroethyl methyl hydrogen phosphite, b.p. 85–87° (3 mm); yield 10.1 g (19%). For constants see table, No. 2.

Found %: P 19.69, 19.78; C 22.46; H 4.98.  $\text{C}_3\text{H}_7\text{O}_3\text{ClP}$ . Calculated %: P 19.56; C 22.76; H 5.09

2-Chloroethyl methyl hydrogen phosphite is a clear, colorless liquid having a feeble unpleasant odor. It is soluble in water, alcohol, ether, benzene, and toluene. The experiment was repeated with other molar ratios of components; no change in yield was observed.

**2-Chloroethyl Diethyl Phosphate.** Over a period of two hours, 55 g of diethyl phosphorochloridate was added to a mixture of 26 g of 2-chloroethanol, 26 g of pyridine, and 25 ml of toluene at 3–5°. The mixture was stirred further for 90 minutes. Pyridine hydrochloride was filtered off, and distillation gave 50 g (72.5%) of 2-chloroethyl diethyl phosphate. For constants see table, No. 3.

Found %: P 14.05, 14.20.  $\text{C}_6\text{H}_{14}\text{O}_4\text{ClP}$ . Calculated %: P 14.32

2-Chloroethyl diethyl phosphate is a clear, colorless liquid with a characteristic ester odor. It is soluble in alcohol, ether, and benzene.

**Bis-2-chloroethyl Methylphosphonate.** Experiment 1. A mixture of 6 g of distilled tris-2-chloroethyl

phosphite and 3.5 g of methyl iodide was heated in a water bath with periodic shaking. At 94° an exothermic reaction set in and the temperature attained 102°. After 20 minutes evolution of heat ceased. The light-yellow liquid was heated in a boiling water bath for a further 20 minutes and then vacuum-distilled. Fraction I, 3.4 g, b.p. 50-52° (38-40 mm), was redistilled and gave 3 g (70%) of 1-chloro-2-iodoethane, b.p. 137°,  $d_4^{20}$  2.1282,  $n_D^{20}$  1.5660 (the literature gives b.p. 140° and  $d_4^{15}$  2.13363). Fraction II, 4.8 g, b.p. 125-126° (4 mm), was redistilled and gave 4.2 g (85%) of bis-2-chloroethyl methylphosphonate. For constants see table, No. 4.

Found %: P 13.70  $C_5H_{11}O_3Cl_2P$ . Calculated %: P 14.03

Bis-2-chloroethyl methylphosphonate is a clear, colorless liquid of unpleasant odor. It is soluble in alcohol, ether, benzene, and toluene, but insoluble in water.

Experiment 2. The reaction was repeated with undistilled tris-2-chloroethyl phosphite prepared by reaction of phosphorus trichloride with 3 molecular proportions of ethylene oxide. No difference was observed in the course of the reaction. The product was 4.1 g (83%) of bis-2-chloroethyl methylphosphonate, b.p. 123-124° (3 mm);  $d_4^{20}$  1.3434;  $n_D^{20}$  1.4676.

Bis-2-chloroethyl Ethylphosphonate. A mixture of 13 g of undistilled tris-2-chloroethyl phosphite and 9.5 g of ethyl iodide was heated in a water bath for four hours and then in an oil bath at 110° for seven hours. Evolution of heat began at a temperature of 108° in the flask, and the temperature of the liquid then rose to 112°. Vacuum distillation of the reaction products gave Fraction I, 5 g, b.p. 50-62° (60 mm), and Fraction II, 8 g (70.5%) of bis-2-chloroethyl ethylphosphonate, b.p. 124-125° (2.5-3 mm). For constants see table, No. 5.

Found %: P 13.2; Cl 30.3  $C_6H_{13}O_3Cl_2P$ . Calculated %: P 13.19; Cl 30.16

Bis-2-chloroethyl ethylphosphonate is a clear, colorless liquid with a feeble unpleasant odor, soluble in alcohol, ether, benzene, and toluene, but insoluble in water.

Bis-2-chloroethyl Acetylphosphonate. Acetyl chloride (9.6 g) was added dropwise to 27 g of undistilled tris-2-chloroethyl phosphite, and the liquid was then heated in a water bath for four hours. Reaction started at 75°, when the temperature of the mixture rose to 87°. Fractionation gave 4.7 g of 1,2-dichloroethane, b.p. 82-83° and  $n_D^{20}$  1.4432 and 13 g (52%) of bis-2-chloroethyl acetylphosphonate, b.p. 138-139° (3-4 mm). For constants see table, No. 6.

Found %: P 12.2; Cl 28.22  $C_6H_{11}O_4Cl_2P$ . Calculated %: P 12.45; Cl 28.47

Bis-2-chloroethyl acetylphosphonate is a clear, colorless, thickish liquid, soluble in alcohol, ether, benzene, and toluene.

2-Chloroethyl Methylphosphonochloridate. The procedure in this synthesis was analogous to that used for the preparation of 2-chloroethyl 2-chloroethylphosphonochloridate [9]. Phosphorus pentachloride (21 g) was added to 11 g of bis-2-chloroethyl methylphosphonate. The mixture was heated at a residual pressure of 90-100 mm in an oil bath, the dichloroethane and phosphoryl chloride formed and excess of phosphorus pentachloride being distilled off. The residue was distilled at 5 mm and gave Fraction I, 3.3 g, b.p. 40-104°, and Fraction II, 7 g, b.p. 103-104°. White crystals which fumed strongly in the air and had b.p. 162-164° rapidly precipitated from Fraction I. This substance was methylphosphonic dichloride. Fraction II, redistilled at 5 mm, gave 4.5 g (50.5%) of pure 2-chloroethyl methylphosphonochloridate. For constants see table, No. 7.

Found %: P 17.37, 17.66; C 20.20, 20.30; H 3.88, 3.81  $C_3H_7O_2Cl_2P$ . Calculated %: P 17.52; C 20.35; H 3.98

This substance is a clear colorless liquid with a sharp odor. It fumes in the air with formation of hydrogen chloride. It is soluble in benzene and toluene.

2-Chloroethyl Methyl Methylphosphonate. Methanol (3.2 g) was added to 15.8 g of 2-chloroethyl methylphosphonochloridate at 19-20°. The reaction time was 30 minutes with a period of further stirring of 30 minutes. Distillation gave 6 g (39%) of 2-chloroethyl methyl methylphosphonate, b.p. 86-88° (1 mm) (No. 8 in table).



Found %: P 18.07, 18.15; C 27.59; H 5.98.  $C_4H_{10}O_3ClP$ . Calculated %: P 17.97; C 27.83; H 5.84

This substance is a clear, colorless liquid with a feeble unpleasant odor. It is soluble in alcohol, ether, benzene and toluene.

2-Chloroethyl Hydrogen Methylphosphonate. 2-Chloroethyl methylphosphonochloridate (11 g) was added dropwise to water with stirring. Removal of excess of water under reduced pressure left 9.8 g of a thick light-yellow odorless noncrystallizing liquid. The yield was quantitative. Titration to phenolphthalein:

Found: acid value 351

$C_3H_8O_3ClP$ . Calculated: acid value 353

This substance is soluble in water and alcohol.

#### SUMMARY

1. An investigation was made of the Arbuzov rearrangement of tris-2-chloroethyl phosphite under the action of methyl iodide, ethyl iodide, and acetyl chloride.

2. Some previously undescribed 2-chloroethyl esters of phosphorous acid and methyl-, ethyl-, and acetyl-phosphonic acids were synthesized.

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## SOME REGULARITIES OBSERVED IN THE CHLORINATION OF ORGANOSILICON COMPOUNDS

V. F. Mironov and V. A. Ponomarenko

Since 1945 the investigation of the chlorination of organosilicon compounds has been given ever-increasing attention. Neglecting a single short note [1] on the possibility of chlorinating hexamethyldisiloxane with the aid of ferric chloride, we may assert that reaction with chlorine and with sulfuryl chloride comprises the two principal methods of chlorinating organosilicon compounds. Initiators for these reactions include ultraviolet radiation, peroxides, and metal chlorides. Chlorination with chlorine may be carried out both in the liquid and in the vapor phases.

Several papers [2-7] have been devoted to liquid-phase chlorination of chloromethylsilanes, and from these it can be concluded 1) that in the liquid phase chlorotrimethylsilane is most readily chlorinated and trichloromethylsilane is least readily chlorinated; 2) that the chloromethyl group formed is chlorinated more readily than the original methyl group (this is the main reason why, in the chlorination of trichloromethylsilane under these conditions,  $\text{ClCH}_2\text{SiCl}_3$  could not be obtained, but only  $\text{Cl}_3\text{CSiCl}_3$  [7]); 3) that in the chlorination of chloromethylsilanes to di- and tri-chloroderivatives the main deciding factor in the orientation of the chlorine (entry of the second chlorine atom into a new methyl or into a chloromethyl group) is the presence of chlorine atoms attached to silicon: the more there are of them, the more likely is the second chlorine atom to enter a chloromethyl group rather than a methyl group.

Liquid-phase chlorination has been carried out also on other organosilicon compounds: methylsiloxanes [8, 9], chlorophenylsilanes [10-12], alkylphenylsilanes [13, 14], trichlorovinylsilane [15], and tetraethylsilane [16-18]. In the chlorination of tetramethylsilane under these conditions, Whitmore and Sommer [19] in 1946 obtained (chloromethyl) trimethylsilane  $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$  in 33% yield.

Somewhat later, Roberts and Dev [20], using conditions of strict vapor-phase chlorination, obtained the same product from tetramethylsilane in a yield of 74%. It has not been found possible to chlorinate chloromethylsilanes  $(\text{CH}_3)_n\text{SiCl}_{(4-n)}$  with  $\text{SO}_2\text{Cl}_2$  under the usual conditions [21, 22]. Sommer [21] and McBride [22] explain these results merely by the deactivating action of chlorosilyl groups. However, attempts to chlorinate tetramethylsilane, which has no chlorosilyl group, with sulfuryl chloride were also unsuccessful [20]. The cause of the lack of success in the chlorination of chloromethylsilanes and tetramethylsilane clearly lies in the low chlorination temperature, at which the decomposition of benzoyl peroxide and the associated chlorination process are rendered difficult. In fact, by raising the reaction temperature with the aid of *o*-dichlorobenzene it was found possible to chlorinate  $\text{CH}_3\text{SiCl}_3$  to  $\text{ClCH}_2\text{SiCl}_3$ , though only, it must be admitted, to the extent of 2.6% [6]. In a medium of chlorobenzene, chlorotrimethylsilane and dichlorodimethylsilane are chlorinated considerably more readily by sulfuryl chloride [22, 23].

As Sommer, Whitmore, and other investigators showed, unlike chloromethylsilanes and tetramethylsilane, chloroethylsilanes [21, 24, 25], tetraethylsilane [26], trichloropropylsilane [27] trichloroisopropylsilane [28], tert-butyltrichlorosilane [29], benzyltrichlorosilane [21], benzyltrimethylsilane and (diphenylmethyl) trimethylsilane [14], and trichloro (1- and 2-chloroethyl) silanes [25] are very readily chlorinated by sulfuryl chloride to monochloro derivatives without the use of any high-boiling solvent. It is clear that these facts led Sommer and Whitmore [21] to the conclusion that chlorination with sulfuryl chloride is considerably more convenient than photochemical chlorination with chlorine, although the photochemical chlorination of ethyl-, propyl-, and other alkyl-chlorosilanes had not in fact been studied. Moreover, in the case of chloromethylsilanes, in spite of fairly

abundant experimental data, it was not clear what conditions of chlorination with chlorine were most favorable for the preparation of monochloro derivatives. The clearest example of this is the difficulty of obtaining  $\text{ClCH}_2\text{SiCl}_3$  from  $\text{CH}_3\text{SiCl}_3$  [6, 7].

The object of our investigation was a more detailed study of the photochemical chlorination of organosilicon compounds with chlorine and sulfuryl chloride and also the systematization of the experimental data that

TABLE 1

Chlorination of Chloromethylsilanes

No.	Compound	Yield of monochloro-derivative (%)		
		Liquid-phase chlorination	Chlorination under Speier's conditions	Chlorination under our conditions
1	$\text{CH}_3\text{SiCl}_3$	0	22	53
2	$(\text{CH}_3)_2\text{SiCl}_2$	67	42	80
3	$(\text{CH}_3)_3\text{SiCl}$	62	51	77
4	$(\text{CH}_3)_4\text{Si}$	33	—	74*
5	$(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$	78	—	88

\*Roberts and Dev [20] carried out the chlorination in a true vapor-phase with removal of monochloro derivatives from the reaction zone.

has now accumulated on this question. Some results of this work have already been published in a series of communications [26, 30-34], in which we have already the superiority of the method of photochemical chlorination with removal of the monochloro derivatives from the reaction zone. In Tables 1-3 we give a comparison of all our results with data from the literature.

This comparison enables us to make the following comments.

1. Chlorination of chloromethylsilanes and tetramethylsilane with chlorine under conditions ensuring removal of monochloro derivatives from the reaction zone gives higher yields than liquid-phase chlorination in which these conditions do not obtain. The necessity for the establishment of such conditions in chlorination to monochloro derivatives follows logically from the data on rates of chlorination of methyl and chloromethyl groups, which are discussed above. This view is already fairly clearly expressed in Speier's patents [35]. However, as will be seen from Table 1, the yields of monochloro derivatives claimed in these patents are comparatively low. In the light of this discussion it can be understood why Whitmore and Sommer [19] obtained only 33% of  $\text{ClCH}_2\text{Si}(\text{CH}_3)_3$  in the liquid-phase chlorination of  $(\text{CH}_3)_4\text{Si}$ , whereas Roberts and Dev [20] attained 74% yield. The important point is not that Roberts and Dev chlorinated  $(\text{CH}_3)_4\text{Si}$  under strictly vapor-phase conditions, which they in fact attained, but that they applied the principle of removing the  $\text{ClCH}_2\text{Si}(\text{CH}_3)_3$  formed from the reaction zone. From the diagram of the apparatus to which they make reference [36] it can be seen that, between the flask containing the original  $(\text{CH}_3)_4\text{Si}$  and the chlorination zone, there was placed a rectification column which did not allow the  $\text{ClCH}_2\text{Si}(\text{CH}_3)_3$  formed to find its way into the chlorination zone. The view that we discussed above finds its clearest confirmation in the example of the successful chlorination of trichloromethylsilane, in which we obtained trichloro (chloromethyl) silane in a yield of more than 50% [26]. The advantage of chlorinating chloromethylsilanes and tetramethylsilane under these conditions, rather than in the liquid-phase — particularly with sulfuryl chloride — will be obvious.

2. In the more complex case, i.e., chlorination of ethyl-, propyl-, and isopropyl-chlorosilanes, photochemical chlorination with chlorine with application of the removal principle again gives results that are not worse than those obtained with sulfuryl chloride, although in the latter case it appears to be possible to carry out the reaction more rapidly.

TABLE 2

Chlorination of Chloroalkylsilanes and Chlorodisilaalkanes

No.	Compound	Yield of monochloro-derivative (%)	
		Chlorination with $\text{SO}_2\text{Cl}_2$	Chlorination with $\text{Cl}_2$
1	$\text{CH}_3\text{CH}_2\text{SiCl}_3$	90	72-86
2	$\text{CH}_3\text{CH}_2\text{SiHCl}_2$	—	55
3	$(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$	40	76
4	$(\text{CH}_3\text{CH}_2)_3\text{SiCl}$	62	81
5	$(\text{CH}_3\text{CH}_2)_4\text{Si}$	50	—
6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SiCl}_3$	90	81
7	$(\text{CH}_3)_2\text{CHSiCl}_3$	33	92
8	$(\text{CH}_3)_2\text{CHCH}_2\text{SiCl}_3$	—	77
9	$(\text{CH}_3)_3\text{CSiCl}_3$	40	—
10	$\text{Cl}_3\text{SiCH}_2\text{SiCl}_3$	7	40
11	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$	40	94
12	$\text{ClCH}_2\text{Si}(\text{CH}_3)_3$	—	88
13	$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$	72	92.5
14	$\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$	63	88.5

Some discussion must be given also of the data in Table 3, from which it will be seen that in chlorination, either with chlorine or with sulfuryl chloride, with reduction in the number of silicon-attached chlorines and

TABLE 3

Relative Amounts of Isomers in the Chlorination of Chloroalkylsilanes

No.	Compound	Chlorination with $\text{SO}_2\text{Cl}_2$			Chlorination with $\text{Cl}_2$		
		$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
1	$\text{CH}_3\text{CH}_2\text{SiCl}_3$	1	2.5	—	1	1.6—1.8	—
2	$\text{CH}_3\text{CH}_2\text{SiHCl}_2$	—	—	—	1	1.5	—
3	$(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$	1	1.7	—	1	1.1	—
4	$(\text{CH}_3\text{CH}_2)_2\text{SiCl}$	1	0.8	—	1	0.7	—
5	$(\text{CH}_3\text{CH}_2)_3\text{Si}$	1	0	—	—	—	—
6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SiCl}_3$	1	3.5	3.1	0	1	0.6
7	$(\text{CH}_3)_2\text{CHSiCl}_3$	1	3.4	—	1	2	—
8	$(\text{CH}_3)_2\text{CHCH}_2\text{SiCl}_3$	—	—	—	1	1.3	5.1
9	$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$	0	1	—	—	—	—
10	$\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$	1	1	—	1	0.6	—

increase in the number of silicon-attached ethyls, the yield of  $\alpha$ -chloro derivatives increases and the yield of  $\beta$ -chloro derivatives correspondingly decreases [30]. Thus, whereas in the case of  $\text{C}_2\text{H}_5\text{SiCl}_3$  the  $\beta$ -chloro derivative predominates, in the case of  $\text{C}_2\text{H}_5\text{Si}(\text{C}_2\text{H}_5)_3$  almost exclusively  $\alpha$ -chlorination occurs [26, 30]. It is notable also that there is a fairly distinct difference in the relative amounts of  $\alpha$ - and  $\beta$ -chloro derivatives between chlorination with chlorine and with sulfuryl chloride: in the latter case the relative yield of the  $\beta$ -chloro derivative is always greater than for the chlorination of the same compound with chlorine. Chlorine attacks a C—H of a silicon-attached methylene group more readily than sulfuryl chloride does [30].

This last fact, and also the marked difference in the actions of chlorine and sulfuryl chloride on chloromethylsilanes, is evidently general in character. In the chloromethylsilanes this general character is shown in the fact that chlorine chlorinates a silicon-attached methyl considerably more readily than sulfuryl chloride does and the rate of chlorination of the methyl group, either by chlorine or by sulfuryl chloride, increases as we pass from  $\text{CH}_3\text{SiCl}_3$  to  $(\text{CH}_3)_3\text{SiCl}$ . The cause of these peculiar features of the chlorination of chloroalkylsilanes evidently lies not so much in the chlorination conditions (temperature, activation conditions, medium, etc.), as in the structural peculiarities of the reacting molecules.

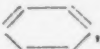
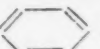
One of the principal peculiarities of the structure of alkylchlorosilanes which can explain the above-mentioned facts consists in the presence of silicon-attached chlorine atoms (the chlorosilyl group  $\text{Cl}_n\text{Si}$ , in which  $n = 1-3$ ). In the case of chloromethylsilanes, the presence of this group leads to a reduction in the rate of chlorination of silicon-attached methyls and to an increase in the rate of chlorination of chloromethyl groups as  $n$  increases. This is most clearly seen in  $\text{Cl}_3\text{SiCH}_3$  and  $\text{Cl}_3\text{SiCH}_2\text{Cl}$ . In the compounds formed by replacing chlorines in  $\text{Cl}_3\text{SiCH}_2\text{Cl}$  by methyls, the way in which a second chlorine atom enters is determined by  $n$ . For example, whereas  $\text{CH}_3\text{SiCl}_2\text{CH}_2\text{Cl}$  gives only  $\text{CH}_3\text{SiCl}_2\text{CHCl}_2$ ,  $(\text{CH}_3)_2\text{SiClCH}_2\text{Cl}$  gives both  $(\text{ClCH}_2)_2\text{SiClCH}_3$  and  $(\text{CH}_3)_2\text{SiClCHCl}_2$ .

In the case of ethyl- and other alkyl-chlorosilanes, the effect of the chlorosilyl group is shown also in a reduction in the rate of chlorination of a silicon-attached methylene group and an increase in the amount of  $\beta$ -derivative as the number of silicon-attached chlorines increases. This  $\beta$ -orientation effect of the chlorosilyl group is most clearly shown in  $\text{Cl}_3\text{SiCH}_2\text{CH}_3$  and  $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{Cl}$ , and it disappears in the case of  $(\text{C}_2\text{H}_5)_4\text{Si}$ . The orienting effect of the chlorosilyl group appears in chlorination both with chlorine and with sulfuryl chloride, but in the latter case it is shown much more clearly [30].

3. The regularities that we have considered are present also in the chlorination of trichloro(1- and 2-chloroethyl) silanes, although the orienting effect of the  $\text{SiCl}_3$  group appears to be manifested in a more complex manner. In the case of  $\text{Cl}_3\text{SiCH}(\text{Cl})\text{CH}_3$  trichloro 1,1-dichloroethyl- and trichloro 1,2-dichloroethyl-silanes are formed in the ratio 1 : 1, whereas in the chlorination of  $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{Cl}$  only trichloro (2,2-dichloroethyl)-silane is formed [25, 32].



4. The close analogy in character between the orienting effects of the  $\text{SiCl}_3$  and  $\text{CF}_3$  groups, which is shown particularly clearly in the chlorination of  $\text{Cl}_3\text{SiCH}_2\text{CH}_3$  and  $\text{F}_3\text{CCH}_2\text{CH}_3$  [37], gave us reason to suppose that also

in the chlorination of  $\text{Cl}_3\text{Si}$  , (cf.  $\text{F}_3\text{C}$  )

the trichlorosilyl group would be meta-orienting. However, according to Yakubovich and Motsareva [10], chlorination of trichlorophenylsilane with chlorine at 50-125° in presence of catalysts ( $\text{Fe}$ ,  $\text{SbCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{I}_2$ ) results in the formation of trichloro-p-chlorophenylsilane, i.e., under these conditions the  $\text{SiCl}_3$  group exhibits an unusual para-orienting effect. In absence of catalysts  $\text{Cl}_3\text{SiC}_6\text{H}_5$  is not chlorinated even at 200° [10].

However, photochemical chlorination of trichlorophenylsilane at 200°, in which the orienting effect of the  $\text{SiCl}_3$  group is not complicated by the influence of catalysts of the Friedel-Crafts type, results in the formation mainly of trichloro-m-chlorophenylsilane [37]: the relative amounts of ortho, meta, and para isomers are 1 : 2.5 : 1. Hence, under conditions of photochemical chlorination at 200° the  $\text{SiCl}_3$  group is a feeble meta-orienting group, which is fully in accord with its orienting effect in the chlorination of the above-discussed alkylchlorosilanes.

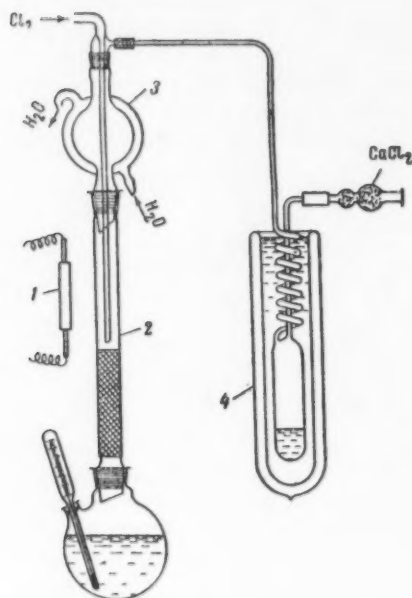
In conclusion, still another interesting fact must be mentioned: the chlorination of dichloroethylsilane  $\text{C}_2\text{H}_5\text{SiHCl}_2$  we succeeded in isolating a small amount of dichloro-1-chloroethylsilane, in which — in spite of the severe conditions of chlorination — the extremely reactive Si-H link was still preserved.

All the above discussion on the photochemical chlorination of alkylchlorosilanes and chlorodisilaalkanes with chlorine and with sulfonyl chloride leads to the conclusion that application of the principle of removal of monochloro derivatives from the reaction zone makes it possible to chlorinate a fairly wide range of organosilicon compounds, including those which cannot be chlorinated — or can be chlorinated only with great difficulty — with the aid of sulfonyl chloride. In spite of certain differences in the character of chlorination with chlorine and with sulfonyl chloride, in both methods definite regularities are observed in the behavior of the organosilicon compounds, and these are associated with the effect of the chlorosilyl group.

## EXPERIMENTAL

**1. Apparatus and Chlorination Procedure.** All the compounds were chlorinated in the apparatus represented in the Figure. The chlorine was first dried by passage through concentrated sulfuric acid in a Tishchenko vessel. The rate at which chlorine was passed was determined by the rate at which the organosilicon compound underwent chlorination. As a rule, an excess of chlorine was passed. The liquid products carried away by the excess of chlorine and the liberated hydrogen chloride was trapped in a vessel immersed in a mixture of acetone and solid carbon dioxide. Completion of chlorination was determined by the temperature in the flask containing the substance being chlorinated. If burning commenced in the chlorination zone, the end of the tube through which the chlorine entered was immersed in the filling and the quartz lamp was moved from the chlorination zone; this always stopped the burning.

The filling in the quartz tube consisted of glass or porcelain rings, 4-5 mm in diameter. It is possible to use a finer filling, and also fillings of metal rings or of other types, but reduction in diameter leads to difficulty in regulating percolation. In the case of high-boiling compounds the length of the tube occupied by filling was insulated. The flask containing the substance being chlorinated was heated in such a way that there was a considerable downflow through the filling in the chlorination zone. A PRK-2 or PRK-4 quartz lamp was



1) quartz lamp; 2) quartz tube with filling;  
3) condenser; 4) trap in a Dewar vessel.



used as source of ultraviolet radiation. Chlorination with sulfuryl chloride was carried out under conditions similar to those described by Sommer and Whitmore [21]. By way of examples we shall describe the chlorination of trichloromethylsilane and dichlorodimethylsilane.

2. Chlorination of Trichloromethylsilane  $\text{CH}_3\text{SiCl}_3$ . Trichloromethylsilane (300 g) was placed in the flask of the chlorination apparatus. When a copious back flow from the reflux condenser was established, the quartz lamp was switched on and chlorine was passed into the chlorination zone at a rate of 60-100 bubbles per minute. When the temperature in the flask attained 110-112°, which required 22 hours, chlorination was stopped. Fractionation through a 20-plate column gave 1) 99 g of unchanged  $\text{CH}_3\text{SiCl}_3$ , b.p. 65.5°; 2) 125 g of trichloro(chloromethyl)silane  $\text{ClCH}_2\text{SiCl}_3$ , b.p. 117-118.5° (53% yield on the amount of  $\text{CH}_3\text{SiCl}_3$  that reacted). In the chlorination of  $\text{CH}_3\text{SiCl}_3$  a considerable amount of higher-boiling chloro derivatives was always formed, particularly  $\text{Cl}_2\text{CHSiCl}_3$ . Thus, in one experiment, as well as 325 g of  $\text{ClCH}_2\text{SiCl}_3$ , 118 g of  $\text{Cl}_2\text{CHSiCl}_3$  was formed; a little  $\text{Cl}_3\text{CSiCl}_3$  was also obtained.

3. Chlorination of Dichlorodimethylsilane  $(\text{CH}_3)_2\text{SiCl}_2$ . In a similar way, 1893 g of  $(\text{CH}_3)_2\text{SiCl}_2$  was chlorinated; the process required 80 hours. The chlorination was stopped when the temperature

TABLE 4

Results of the Chlorination of Alkylchlorosilanes

No.	Original compounds	Isolated chlorination products	Amount of original compound (g)	Duration of chlorination (hours)	Final temperature (°C)	Yield of monochloro derivative (%)
1	$\text{CH}_3\text{SiCl}_3$	$\text{ClCH}_2\text{SiCl}_3$ $\text{Cl}_2\text{CHSiCl}_3$	300	22	112	53
2	$(\text{CH}_3)_2\text{SiCl}_2$	$\text{ClCH}_2\text{Si}(\text{Cl})_2\text{CH}_3$ $\text{Cl}_2\text{CHSi}(\text{Cl})_2\text{CH}_3$ $\text{Cl}_2\text{CHSi}(\text{Cl})_2\text{CH}_3$	1893	80	112	80
3	$(\text{CH}_3)_3\text{SiCl}$	$\text{ClCH}_2\text{Si}(\text{Cl})(\text{CH}_3)_2$	272	8	110	77
4	$(\text{C}_2\text{H}_5)_3\text{SiCl}$	$\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$ $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ $\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$	376	17	136	86
5	$(\text{C}_2\text{H}_5)_2\text{SiCl}_2$	$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ $\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$ $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ $\text{CH}_3\text{CH}(\text{Cl})\text{SiHCl}_2$ $\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$	370	58	140	55
6	$(\text{C}_2\text{H}_5)_3\text{SiCl}$	$(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$ $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ $(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$	369	51.5	160	76
7	$(\text{C}_2\text{H}_5)_3\text{SiCl}$	$(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$ $\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$ $(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$ $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ $(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$	150	23.5	190	81
8	$(\text{C}_2\text{H}_5)_4\text{Si}$	$\text{CH}_3\text{CHSi}(\text{C}_2\text{H}_5)_3$ $\text{Cl}$ $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{SiCl}_3$ $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3$ $(\text{CH}_3)_2\text{C}(\text{Cl})\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{SiCl}_3$ $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{SiCl}_3$ $(\text{CH}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$	503*	—	—	50*
9	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SiCl}_3$	$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{SiCl}_3$ $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3$ $(\text{CH}_3)_2\text{C}(\text{Cl})\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{SiCl}_3$ $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{SiCl}_3$ $(\text{CH}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$	1200	35	160	89
10	$(\text{CH}_3)_2\text{CHSiCl}_3$	$(\text{CH}_3)_2\text{C}(\text{Cl})\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{SiCl}_3$ $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{SiCl}_3$ $(\text{CH}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$	1050	70	148	80
11	$(\text{CH}_3)_2\text{CHCH}_2\text{SiCl}_3$	$(\text{CH}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$ $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $(\text{CH}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$	356	28	174	77
12	$\text{Cl}_2\text{SiCH}_2\text{SiCl}_3$	$\text{Cl}_3\text{SiCH}(\text{Cl})\text{SiCl}_3$ $\text{Cl}_3\text{SiC}(\text{Cl})_2\text{SiCl}_3$ $\text{Cl}_3\text{SiCH}(\text{Cl})\text{CH}_2\text{SiCl}_3$	303 141* 343	17 — 22	208 — 221	— 7* 94
13	$\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{SiCl}_3$	$\text{Cl}_3\text{SiCH}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{Cl}_3\text{SiC}(\text{Cl})\text{CH}_2\text{SiCl}_3$ $\text{Cl}_3\text{SiCH}(\text{Cl})\text{CH}_2\text{SiCl}_3$	169* — 255	— — 42	— — 226	40* — 83
14	$\text{C}_6\text{H}_5\text{SiCl}_3$	Mix. o-, m- and p- $\text{ClC}_6\text{H}_4\text{SiCl}_3$	255	42	226	83
15	$\text{ClCH}_2\text{Si}(\text{CH}_3)_3$	$\text{Cl}_2\text{CHSi}(\text{CH}_3)_3$ $(\text{ClCH}_2)_2\text{Si}(\text{CH}_3)_2$ $\text{ClCH}_2\text{CH}(\text{Cl})\text{SiCl}_3$ $\text{Cl}_2\text{CHCH}_2\text{SiCl}_3$ $\text{CH}_3\text{C}(\text{Cl})_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{Cl})\text{SiCl}_3$	154	20	135	88
16	$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$	$\text{ClCH}_2\text{CH}(\text{Cl})\text{SiCl}_3$ $\text{Cl}_2\text{CHCH}_2\text{SiCl}_3$ $\text{CH}_3\text{C}(\text{Cl})_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{Cl})\text{SiCl}_3$	1265	53	174	92.5
17	$\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$	$\text{CH}_3\text{C}(\text{Cl})_2\text{SiCl}_3$ $\text{ClCH}_2\text{CH}(\text{Cl})\text{SiCl}_3$	482	18	151	88.5

\*Results on chlorination with sulfuryl chloride.


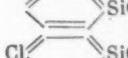

in the flask rose to 112°. Fractionation through a 20-plate column gave:

1. 396 g of unchanged  $(\text{CH}_3)_2\text{SiCl}_2$ , b.p. 69.5°;
2. 1520 g of dichloro(chloromethyl)methylsilane  $\text{ClCH}_2\text{Si}(\text{Cl})\text{CH}_3$ , b.p. 120.6-121.2°; 80% yield on the amount of  $(\text{CH}_3)_2\text{SiCl}_2$  that reacted;
3. 170 g of dichloro(dichloromethyl)methylsilane  $\text{Cl}_2\text{CHSi}(\text{Cl})_2\text{CH}_3$ , b.p. 148-149°.
4. 35 g of residue.

When the chlorination of  $(\text{CH}_3)_2\text{SiCl}_2$  was continued until the temperature reached 126°, the amount recovered unchanged was very small, but the yield of  $\text{ClCH}_2\text{Si}(\text{Cl})_2\text{CH}_3$  rose to 88%. This temperature, therefore,

TABLE 5

Constants of Chloro(chloroalkyl)silanes

No.	Chloro compound	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	MR	
					Found	Calc.
1	$\text{ClCH}_2\text{SiCl}_3$	118.0 (743)	1.4441	1.4535	34.46	34.01
2	$\text{Cl}_2\text{CHSiCl}_3$	143.5 (747)	1.5518	1.4714	39.22	38.88
3	$\text{ClCH}_2\text{Si}(\text{Cl})_2\text{CH}_3$	121.0 (750)	1.2842	1.4495	34.18	34.38
4	$\text{Cl}_2\text{CHSi}(\text{Cl})_2\text{CH}_3$	148.5 (750)	1.4116	1.4700	39.12	39.22
5	$\text{ClCH}_2\text{Si}(\text{Cl})(\text{CH}_3)_2$	114 (752)	1.0862	1.4368	34.48	34.75
6	$\text{ClCH}_2\text{Si}(\text{CH}_3)_3$	97.3 (740)	0.8791	1.4180	35.18	35.12
7	$\text{Cl}_2\text{CHSi}(\text{CH}_3)_3$	133 (730)	—	—	—	—
8	$(\text{ClCH}_2)_2\text{Si}(\text{CH}_3)_2$	160 (730)	—	—	—	—
9	$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$	151.7 (751)	1.4239	1.4652	38.45	38.64
10	$\text{CH}_3\text{CH}(\text{Cl})\text{SiCl}_3$	136.5 (747)	1.3912	1.4545	38.56	38.64
11	$\text{CH}_3\text{CH}(\text{Cl})\text{SiHCl}_2$	115-116	1.2614	1.4484	34.72	34.64
12	$\text{CH}_3\text{CH}(\text{Cl})\text{Si}(\text{Cl})_2\text{C}_2\text{H}_5$	41.5 (9)	1.2017	1.4578	43.47	43.64
13	$\text{ClCH}_2\text{CH}_2\text{Si}(\text{Cl})_2\text{C}_2\text{H}_5$	60.5 (9.5)	1.2174	1.4678	43.72	43.64
14	$\text{CH}_3\text{CH}(\text{Cl})\text{Si}(\text{Cl})(\text{C}_2\text{H}_5)_2$	79.5-80 (27.5)	1.0406	1.4562	—	—
15	$\text{ClCH}_2\text{CH}_2\text{Si}(\text{Cl})(\text{C}_2\text{H}_5)_2$	97.0-97.5 (27.5)	1.0555	1.4639	—	—
16	$\text{CH}_3\text{CH}(\text{Cl})\text{Si}(\text{C}_2\text{H}_5)_3$	194.6 (750)	—	1.4535	—	—
17	$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{SiCl}_3$	157 (740)	—	—	—	—
18	$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{SiCl}_3$	162 (744)	1.3410	1.4600	43.29	43.27
19	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3$	178.4 (750)	1.3590	1.4668	43.26	43.27
20	$(\text{CH}_3)_2\text{C}(\text{Cl})\text{SiCl}_3$	151 (750)	b.p. 110°	—	—	—
21	$\text{ClCH}_2\text{CH}(\text{CH}_3)\text{SiCl}_3$	164 (744)	1.3520	1.4670	43.42	43.27
22	$(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{SiCl}_3$	161-164	1.2665	1.4668	49.50	47.90
23	$(\text{CH}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{SiCl}_3$	179.5 (740)	1.3110	1.4660	47.74	47.90
24	$\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$	192.0 (740)	1.3114	1.4680	47.92	47.90
25	$\text{Cl}_3\text{SiCH}(\text{Cl})\text{SiCl}_3$	210.5- —211.2 (757)	—	1.4916	—	—
26	$\text{Cl}_3\text{SiC}(\text{Cl})_2\text{SiCl}_3$	227.5 (756)	—	1.5010	—	—
27	$\text{Cl}_3\text{SiCHClCH}_2\text{SiCl}_3$	225.0 (737)	1.5774	1.4915	60.89	61.05
28	$\text{Cl}_2\text{CHCH}_2\text{SiCl}_3$	175 (740)	1.5201	1.4800	43.43	43.48
29	$\text{ClCH}_2\text{CH}(\text{Cl})\text{SiCl}_3$	181 (760)	1.5156	1.4850	43.94	43.48
30	$\text{CH}_3\text{C}(\text{Cl})_2\text{SiCl}_3$	151.8 (745)	—	—	—	—
31		240.5 (742.5)	1.4629	1.5510	53.64	53.83
32		230.5 (738)	1.4384	1.5421	53.84	53.83
33		232.5 (745.5)	1.4316	1.5418	54.00	53.83

must be regarded as the optimum for obtaining a maximum yield of  $\text{ClCH}_2\text{Si}(\text{Cl})\text{CH}_3$ . When chlorination was continued until the temperature reached 150°, the main reaction product was  $\text{ClCH}_2\text{Si}(\text{Cl})\text{CH}_3$ . Thus, 563 g of  $(\text{CH}_3)_2\text{SiCl}_2$  then gave 75 g of  $\text{ClCH}_2\text{Si}(\text{Cl})_2\text{CH}_3$ ,\* 430 g of  $\text{Cl}_2\text{CHSi}(\text{Cl})_2\text{CH}_3$  and 103 g of trichloro derivatives boiling in the range 155-165°. No unchanged  $(\text{CH}_3)_2\text{SiCl}_2$  was isolated.

\*As in original; presumably  $\text{ClCH}_2\text{Si}(\text{Cl})_2\text{CH}_3$  is intended — Publisher's note

Other compounds were chlorinated under similar conditions. The results of the chlorination of all the compounds that we studied are presented in Table 4. The physical properties of the monochloro derivatives obtained are presented in Table 5.

#### SUMMARY

1. A general method of photochemical chlorination of alkylchlorosilanes and chlorodisilaalkanes was studied for numerous cases. It gives high yields of monochloro derivatives, this being attained by carrying out the chlorination in a simple apparatus in which the monochloro derivative formed is continuously removed from the reaction zone and does not again come into contact with chlorine.

2. It was shown that this method of chlorination has advantages over chlorination with sulfuryl chloride, both as regards generality and as regards the high yield and purity of the monochloro derivatives formed. The method has advantages also over chlorination in the liquid phase, and these are particularly notable in the preparation of the previously inaccessible  $\text{ClCH}_2\text{SiCl}_3$  from  $\text{CH}_3\text{SiCl}_3$ .

3. On the basis of our own results and data in the literature, the main laws governing chlorination, both with chlorine and with sulfuryl chloride, were formulated.

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\* Original Russian pagination. See C. B. Translation.

## SYNTHESIS OF STEROIDS AND RELATED COMPOUNDS

### COMMUNICATION 39. STEROID ANALOGS NOT CONTAINING

#### RING B

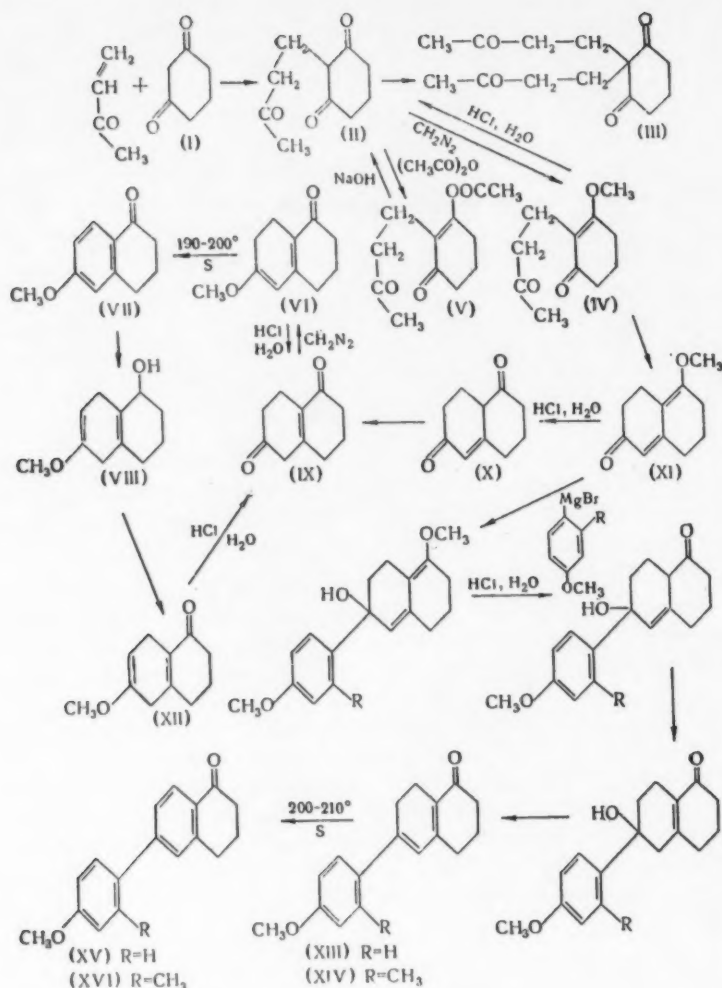
I. N. Nazarov and S. I. Zavyalov

In a previous paper [1] we described the synthesis of a series of steroid analogs not containing ring B. In the development of these investigations we worked out a new method of synthesizing tricyclic ketones of types (XIII) and (XIV), which are of interest not only as model steroid analogs, but, with suitable choice of substituents, as possible intermediate products in the synthesis of actual steroids.

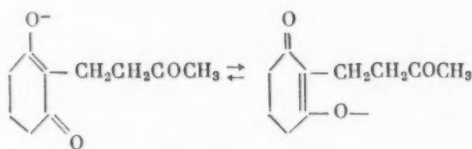
As already noted [2], in the condensation of 3-buten-2-one with 1,3-cyclohexanedione (I), the acidic triketone (II) is formed together with a neutral disubstituted condensation product (III), which is readily separated by treatment with sodium carbonate solution. A mixture of these substances is formed also when equivalent amounts of the reactants are used; in this case the triketone (II) is contaminated with a considerable amount of unchanged 1,3-cyclohexanedione, which cannot be removed by vacuum distillation. For the preparation of the triketone (II) in the pure state, the acid reaction products were treated with ethereal diazomethane and the resulting mixture of enol ethers was readily resolved by vacuum fractionation. When hydrolyzed with 3% hydrochloric acid, the enol ether (IV) was converted quantitatively into the crystalline triketone (II), and treatment with excess of 2,4-dinitrophenylhydrazine in the cold gave the mono-2,4-dinitrophenylhydrazone, a red substance having  $\lambda_{\max} = 385 \text{ m}\mu$  (in methanol) and evidently having its free keto group in the butyl chain. The pure triketone (II) can be prepared also through the corresponding enol acetate (V), which is formed when the acid reaction products are boiled with acetic anhydride.

When the enol ether (IV) was allowed to stand at room temperature for three hours in presence of potassium tert-butoxide dissolved in benzene and tert-butyl alcohol, it underwent cyclization and was converted in 61% yield into the bicyclic methoxy ketone (XI). Increase in time of standing and raising of the reaction temperature led to a lower yield of the methoxy ketone (XI) owing to resinification and formation of by-products of acidic character. When treated with excess of 2,4-dinitrophenylhydrazine in methanol solution in presence of traces of hydrochloric acid, the methoxy ketone (XI) underwent hydrolysis followed by formation of the bis-2,4-dinitrophenylhydrazone of the diketone (IX), which we had prepared in our laboratory by hydrolysis of the isomeric methoxy ketone (XII) [3]. This last compound is formed, as described previously [3], by the reduction of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (VII) with sodium in liquid ammonia and subsequent oxidation of the corresponding alcohol (VIII) with aluminum isopropoxide. The triketone (II) itself did not undergo cyclization even after treatment for many hours with potassium tert-butoxide. Neither could the cyclization of the enol acetate (V) be brought about under these conditions, since it was hydrolyzed by potassium tert-butoxide with formation of the triketone (II). The inability of the triketone (II) to undergo an intramolecular





crotonic condensation under the conditions studied is probably to be explained by the weakening of the ketone character of both keto groups as a result of the establishment of an equilibrium between two ionic forms:



Hydrolysis of the methoxy ketone (XI) with dilute hydrochloric acid was accompanied by displacement of the double bond into the intercycle position ( $X \rightarrow IX$ ) and resulted in the formation of crystalline 3,4,7,8-tetrahydro-1,6-(2H,5H)-naphthalenedione (IX) in high yield. In order to prove the position of the double bond in the diketone (IX), this compound was treated with diazomethane and converted into the enol ether (VI), dehydrogenation of which with sulfur at 190–200° gave the known 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (VII) [4].



Treatment of the methoxy ketone (XI) with *p*-methoxyphenylmagnesium bromide in ethereal solution and subsequent hydrolysis, isomerization, and dehydration of the product of the Grignard reaction gave the dienic ketone (XIII), which we have prepared previously by another method [1]. Under the same conditions, 4-methoxy-*o*-tolylmagnesium bromide and the methoxy ketone (XI) gave the methyl homolog (XIV), the structure of which was confirmed by its conversion into a derivative of 3,4-dihydro-1(2H)-naphthalenone (XVI) by a short treatment with sulfur at 200–210°. The dienic ketones (XIII) and (XIV) form 2,4-dinitrophenylhydrazones of a black-violet color, whereas those of the corresponding 3,4-dihydro-1(2H)-naphthalenones are red. It is interesting to note that the dienic ketone (XIII) is bright yellow, whereas its methyl homolog (XIV) is almost colorless, which evidently indicates a lower degree of conjugation in the molecule of the latter substance owing to disturbance of the coplanarity of its dihydrobiphenyl system.

#### EXPERIMENTAL

Condensation of 3-Buten-2-one with 1,3-Cyclohexanedione. A methanol solution of 32 g of 3-buten-2-one was added to a stirred solution of 60 g of 1,3-cyclohexanedione and 5 g of sodium carbonate in 200 ml of water. The mixture was heated for 30 minutes at 80–85° and, after being cooled, it was treated with excess of sodium carbonate solution and extracted with chloroform. The extract yielded 12 g of 2,2-bis-3-oxobutyl-1,3-cyclohexanedione (III), m.p. 123–124° [2]. The alkaline solution was acidified with dilute hydrochloric acid, and chloroform extraction then gave 66 g of a mixture of 2-(3-oxobutyl)-1,3-cyclohexanedione (II) and unchanged 1,3-cyclohexanedione.

Preparation of the Methyl Ether of the Enol Form of 2-(3-Oxobutyl)-1,3-cyclohexanedione (IV). The above mixture (66 g) and the calculated amount of 3% ethereal diazomethane were mixed and set aside at room temperature for three hours. Removal of ether and vacuum distillation of the residue gave 14 g of the methyl ether of the enol form of 1,3-cyclohexanedione, b.p. 123–124° (19 mm);  $n_D^{20}$  1.5135 [5], and 35 g of the methyl ether of the enol form of 2-(3-oxobutyl)-1,3-cyclohexanedione (IV), b.p. 158–160° (1 mm) and m.p. 41–42° (from ether).

Found %: C 67.08, 67.27; H 8.21, 8.27  $C_{11}H_{16}O_3$ . Calculated %: C 67.3; H 8.2

The 2,4-dinitrophenylhydrazone of (IV) melted at 218–220°.

Found %: N 15.32; 15.23,  $C_{17}H_{20}N_4O_6$ . Calculated %: N 14.9

When hydrolyzed with 3% hydrochloric acid in the cold, the enol ether (IV) was converted quantitatively into 2-(3-oxobutyl)-1,3-cyclohexanedione (II), m.p. 104–106° (from a benzene-heptane mixture).

Found %: C 65.45, 65.64; H 7.61, 7.67  $C_{10}H_{14}O_3$ . Calculated %: C 65.9; H 7.7

Preparation of the Acetic Ester of the Enol Form of 2-(3-Oxobutyl)-1,3-cyclohexanedione (V). The above-described mixture (4 g) of 2-(3-oxobutyl)-1,3-cyclohexanedione (II) and 1,3-cyclohexanedione (I) was boiled with 20 ml of acetic anhydride for one hour. Vacuum fractionation gave 2 g of the acetic ester of the enol form of 2-(3-oxobutyl)-1,3-cyclohexanedione (V), b.p. 155–160° (1 mm) and  $n_D^{20}$  1.5010.

Found %: C 64.53, 64.68; H 7.23, 7.31  $C_{12}H_{16}O_4$ . Calculated %: C 64.3; H 7.1

When hydrolyzed with dilute alkali, the enol acetate (V) was converted quantitatively into the triketone (II).

Cyclization of the Enol Ether of 2-(3-Oxobutyl)-1,3-cyclohexanedione. A solution of 4 g of the methyl ether of the enol form of 2-(3-oxobutyl)-1,3-cyclohexanedione (IV) in 10 ml of benzene was added to a stirred solution of potassium *tert*-butoxide prepared from 0.8 g of potassium and 20 ml of *tert*-butyl alcohol. After standing for three hours at room temperature, the mixture was treated with water and extracted with ether. The extract yielded 2.2 g (61%) of the methoxy ketone (XI), m.p. 63–64° (from heptane).

Found %: C 73.87, 73.84; H 7.88, 7.83  $C_{11}H_{14}O_2$ . Calculated %: C 74.1; H 7.9

When allowed to stand in the air the methoxy ketone (XI) underwent some change, and treatment with excess of 2,4-dinitrophenylhydrazine in methanol solution in presence of hydrochloric acid gave the bis-2,4-dinitrophenylhydrazone of 3,4,7,8-tetrahydro-1,6(2H,5H)-naphthalenedione (IX), m.p. 205-207°, which had been prepared in our laboratory from the methoxy ketone (XII).

Preparation of 3,4,7,8-Tetrahydro-1,6(2H,5H)-naphthalenedione (IX). A mixture of 4.5 g of the methoxy ketone (XI), 15 ml of ether, and 15 ml of 3% hydrochloric acid was shaken at room temperature for three hours. The ether layer was separated, and the aqueous solution was extracted three times with chloroform. The combined extracts yielded 2.9 g (70%) of 3,4,7,8-tetrahydro-1,6(2H,5H)-naphthalenedione (IX), b.p. 145-147° (1 mm) and m.p. 44-45° (from ether), identical with the diketone previously prepared in our laboratory by hydrolysis of the methoxy ketone (XII).

When treated with excess of 2,4-dinitrophenylhydrazine, the diketone (IX) gave the bis-2,4-dinitrophenylhydrazone, m.p. 205-207°, referred to above, and by the action of hydroxylamine acetate in aqueous solution it gave the dioxime, m.p. 183-185° (from aqueous alcohol) [3].

Reaction of 3,4,7,8-Tetrahydro-1,6(2H,5H)-naphthalenedione with Diazomethane. A mixture of (IX) and excess of 3% ethereal diazomethane was left for three hours at room temperature. Removal of solvent resulted in the isolation of 1.7 g (50%) of the methoxy ketone (VI), b.p. 145-148° (1 mm) and  $n_D^{20}$  1.5910.

Found%: C 73.81, 73.90; H 7.71, 7.82.  $C_{11}H_{14}O_2$ . Calculated %: C 74.1; H 7.9

By hydrolysis with 3% hydrochloric acid the methoxy ketone (VI) was converted into the diketone (IX).

Dehydrogenation of the Methoxy Ketone (VI). A mixture of 1.8 g of the methoxy ketone (VI) and 0.3 g of sulfur was heated at 190-200° for 15 minutes. When cool, the mixture was extracted with ether. Vacuum fractionation of the reaction product gave 0.6 g (33%) of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (VII), b.p. 135-138° (2 mm) and m.p. 78-79°, undepressed by admixture of a known sample [4].

Reaction of the Methoxy Ketone (XI) with p-Methoxyphenylmagnesium Bromide. The Grignard reagent prepared from 1.2 g of magnesium, 12 g of p-bromoanisole, and 40 ml of ether was cooled with ice and stirred while a solution of 3.6 g of the methoxy ketone (XI) in 40 ml of ether was added. After standing for 12 hours at room temperature, the mixture was treated with ice and dilute hydrochloric acid and then extracted with ether. The ether extract was washed with dilute alkali, with hydrochloric acid, and with water. When solvent was removed, the residue solidified. The product, amounting to 1.6 g (32%), was the previously described dienic ketone (XIII), m.p. 105-106° (from a benzene-heptane mixture) [1].

Reaction of the Methoxy Ketone (XI) with 4-methoxy-o-tolylmagnesium Bromide. The procedure was as described above. From 1 g of magnesium, 14 g of 4-bromo-3-methylanisole (b.p. 133-135° (40 mm);  $n_D^{20}$  1.5630 [6]), and 3.6 g of the methoxy ketone (XI), 1 g (18%) of the dienic ketone (XIV), m.p. 68-69° (from heptane), was obtained.

Found %: C 80.51, 80.52; H 7.43, 7.42.  $C_{18}H_{20}O_2$ . Calculated %: C 80.6; H 7.5

After being washed with methanol, the 2,4-dinitrophenylhydrazone melted at 190-192°.

Found %: N 12.68; 12.77  $C_{24}H_{24}O_5N_4$ . Calculated %: N 12.5

Dehydrogenation of the Dienic Ketone (XIV). A mixture of 0.4 g of the dienic ketone (XIV) and 0.2 g of sulfur was heated for 15 minutes at 200-210°. When cool, the mixture was dissolved in benzene, treated with alumina, and evaporated down. The residue crystallized when allowed to stand. The product, amounting to 0.12 g (30%), was the 3,4-dihydro-1(2H)-naphthalenone (XVI), m.p. 88-89° (from heptane).

Found %: C 81.28, 81.35; H 6.53, 6.67.  $C_{18}H_{18}O_2$ . Calculated %: C 81.2, H 6.7.

After being washed with methanol, the 2,4-dinitrophenylhydrazone melted at 204-205°.

Found %: N 12.32; 12.41  $C_{24}H_{22}O_5N_4$ . Calculated %: N 12.5

#### SUMMARY

1. By the condensation of 1,3-cyclohexanedione (I) with 3-buten-2-one, a mixture of the 3-oxobutyl derivatives (II) and (III) was formed. By the action of diazomethane on the ketone (II), the pure methyl ether of the enol form of 2-(3-oxobutyl)-1,3-cyclohexanedione (IV) was obtained, and treatment of this with potassium tert-butoxide gave the bicyclic methoxy ketone (XI).

2. Hydrolysis of the methoxy ketone (XI) with dilute hydrochloric acid gave 3,4,7,8-tetrahydro-1,6(2H,5H)-naphthalenedione (IX) in high yield.

3. With diazomethane 3,4,7,8-tetrahydro-1,6(2H,5H)-naphthalenedione (IX) gave the bicyclic methoxy ketone (VI), which was converted by dehydrogenation with sulfur into the known 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (VII).

4. By reaction of p-methoxyphenylmagnesium and 4-methoxy-o-tolylmagnesium bromides with the methoxyketone (XI) and subsequent hydrolysis, isomerization, and dehydration of the reaction products, the dienic ketones (XIII) and (XIV) were obtained. These ketones are of interest as model steroid analogs not containing ring B.

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\*Original Russian pagination. See C. B. Translation.

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## BROMOMETHYLATION OF AROMATIC HYDROCARBONS

I. N. Nazarov and A. V. Semenovskiy

Unlike chloromethylation, bromomethylation has received very little study, although the introduction of the bromomethyl group can undoubtedly be of considerable interest in certain cases. Only a few investigations on the bromomethylation reaction have been reported. The bromomethylation of benzene, toluene, chlorobenzene, and bromobenzene with the aid of bisbromomethyl ether has been described [1]. There are some German patents [2] on the bromomethylation of salicylic acid, salicylaldehyde, anisic ester, and diphenyl ether. Darzens [3] states that bromomethylation and chloromethylation can be regarded as general methods, but the yields of bromomethyl derivatives are always lower than in the case of chloromethylation, which is evidently to be explained by the more ready formation of diarylmethane by-products. Comparison of the rates of reaction of aromatic compounds with chloro- and bromo-methyl ethers in glacial acetic acid showed that bromomethylation is about ten times as fast as chloromethylation [4]. A method has been proposed for bromomethylation in acetic acid with paraform, sodium bromide, and sulfuric acid [5], and this has been applied with success for the bromomethylation of tert-butylbenzene [6].

Having studied the chloromethylation of aromatic hydrocarbons [7], we decided that we should also investigate bromomethylation under analogous conditions. It was found that the bromomethylation of aromatic hydrocarbons, using excess of hydrocarbon or carbon tetrachloride as solvent and paraform and hydrogen bromide as reagent in presence of anhydrous zinc chloride, led to the formation of mono(bromomethyl) derivatives in yields similar to those obtained in chloromethylation. However, when the bromomethylation of toluene, ethylbenzene, and cumene was carried out in concentrated hydrobromic acid in absence of zinc chloride, the yields of the corresponding mono(bromomethyl) derivatives were increased, on the average, to 80%. The success of the bromomethylation process carried out in this way can be attributed to the elimination of anhydrous zinc chloride, which favors the formation of diarylmethane by-products.

In the investigation of the chloromethylation of toluene, ethylbenzene, and cumene, we showed that increase in the bulk of the alkyl substituent in the benzene ring caused the reaction to be greatly displaced in the direction of formation of para isomers owing to screening of the ortho position [7]. No investigation of orientation in the bromomethylation reaction, i.e., of the relative amounts of ortho and para isomers formed, has been reported, apart from sporadic data on exclusive formation of *p*-bromomethyl derivatives [1, 6]. It was therefore of interest to investigate orientation in the bromomethylation of toluene, ethylbenzene, and cumene in order to compare the results with data on the chloromethylation of these hydrocarbons. The establishment of the isomeric composition of the bromomethyl derivatives by oxidation with chromium trioxide in acetic acid (on analogy with the oxidation of mixtures of chloromethyl derivatives) was found to be impossible since the bromine then liberated reacted with formation of bromination by-products. In order to establish the relative amounts of isomers formed in the bromomethylation of toluene, ethylbenzene, and cumene, the bromomethyl derivatives were hydrolyzed and the resulting mixtures of substituted benzyl alcohols, which corresponded in composition to the mixtures of bromomethyl derivatives, were oxidized with chromium trioxide in acetic acid. The results of this oxidation were compared with those of the oxidation of mixtures of substituted benzyl alcohols corresponding to mixtures of chloromethylation products from the same hydrocarbons and with our earlier results [7] on the relative amounts of isomers in the chloromethylation products from toluene, ethylbenzene, and cumene.

Such comparisons show that the chloromethylation and the bromomethylation of these aromatic hydrocarbons give mixtures of halomethylation derivatives of the same composition (Table 1).



In order to obtain direct proof of the formation of *o*-bromomethyl derivatives, the mixtures obtained were oxidized with dilute nitric acid at 200°, as described previously [8]. A good yield (60-80%) was then obtained of a mixture of the corresponding benzenedicarboxylic acids, from which pure phthalic and terephthalic acids were isolated.

TABLE 1

C <sub>6</sub> H <sub>5</sub> R	Chloromethylation products (%)		Bromomethylation products (%)	
	p-isomer	o-isomer	p-isomer	o-isomer
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	48.3	51.7	48.3	51.7
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>3</sub>	77.3	22.7	75.7	24.3
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	87.2	12.8	86.7	13.3

## EXPERIMENTAL

### Bromomethylation of Aromatic Hydrocarbons in presence of Zinc Chloride.

a) Hydrogen bromide was passed for one hour into a vigorously stirred mixture of 150 ml of toluene, 15 g of paraformaldehyde, 8.5 g of anhydrous zinc chloride, and a little phosphorus at a temperature of 50°. The reaction mixture was then stirred further for 20 minutes and filtered, washed with water, with sodium bicarbonate solution, and again with water, and dried over calcium chloride. Toluene (90 ml) and a small head fraction (0.27 g) were distilled off, and vacuum distillation then gave 53.6 g (58%) of a mixture of mono(bromomethyl)-toluenes, b.p. 82-90° (10 mm). A high-boiling fraction (9.6 g), b.p. 145-150° (13 mm) consisted of diarylmethane derivatives. The residue from the distillation amounted to 4.1 g.

b) Hydrogen bromide was passed into a vigorously stirred mixture of 150 ml of carbon tetrachloride, 15 g of paraform, 10 g of anhydrous zinc chloride, and a little phosphorus until the paraform dissolved (35 minutes). Then, at 50° and with continuous passage of hydrogen bromide, 53 g of ethylbenzene was added dropwise over a period of 80 minutes. Passage of hydrogen bromide was then stopped, and the reaction mixture was stirred further for 20 minutes. The solution was filtered, washed with water, with sodium bicarbonate solution, and again with water, and dried over calcium chloride. Carbon tetrachloride and a small head fraction (4.2 g) were distilled off, and vacuum fractionation of the residue gave 48.1 g (48.3%) of a mixture of (bromomethyl) ethylbenzenes, b.p. 96-100° (7.5 mm). The residue, which consisted mainly of diarylmethane derivatives, amounted to 18.8 g.

### Bromomethylation of Aromatic Hydrocarbons in Concentrated Hydrobromic Acid in absence of Zinc Chloride.

a) Hydrogen bromide was passed for six hours into a vigorously stirred mixture of 90 ml of concentrated hydrobromic acid, 70 g of toluene, 30 g of paraform, and a little phosphorus at a temperature of 50°. The reaction mixture was then stirred further at 50° for 19 hours. It was filtered, and the organic layer was separated, washed with water, with sodium bicarbonate solution, and again with water, and dried over calcium chloride. A small head fraction (0.6 g) was distilled off, and vacuum distillation of the residue gave 99 g (71.3%) of a mixture of mono(bromomethyl)toluenes, b.p. 112-120° (23 mm). The high-boiling residue from the distillation amounted to 43.3 g.

b) Under similar conditions—80 g of ethylbenzene, 30 g of paraform and 90 ml of hydrobromic acid, passage of hydrogen bromide for four hours, and stirring of the reaction mixture for a further 21 hours at 50-55°—127.9 g (85%) of a mixture of (bromomethyl)ethylbenzenes, b.p. 101-104° (10 mm), was obtained. The residue from the distillation amounted to 12.5 g.

c) From 60 g of cumene, 20 g of paraform, and 90 ml of hydrobromic acid with passage of hydrogen bromide for 4.5 hours and stirring of the reaction mixture for a further 19.5 hours at 50-55°, we obtained 82.7 g (78%) of a mixture of (bromomethyl)cumenes, b.p. 126-130° (20 mm). The residue from the distillation amounted to 6.4 g.



### Hydrolysis of Chloromethyl Derivatives of Aromatic Hydrocarbons.

The mixture of mono(chloromethyl) derivatives of ethylbenzene (33 g) was stirred in a boiling suspension of 15 g of chalk in 100 ml of water for 25 hours. The reaction mixture was then filtered, the organic layer was separated, the aqueous layer was extracted with ether, and the ether extract combined with the organic layer was dried over anhydrous magnesium sulfate. Ether was distilled off, and vacuum distillation of the residue gave 23.2 g (80%) of a mixture of the corresponding alcohols, b.p. 117-121° (12 mm). The residue from the distillation amounted to 3.8 g.

Similarly, 30.6 g of the mixture of (chloromethyl)cumenes, boiled for 25 hours, gave 17.4 g (64%) of a mixture of the corresponding alcohols, b.p. 126-129° (15 mm).

### Oxidation of Hydroxymethyl Derivatives of Aromatic Hydrocarbons with Chromium Trioxide.

a) A mixture of 3.56 g of the mixture of alcohols obtained by hydrolysis of the bromomethylation product of toluene, 30 g of chromium trioxide, 90 ml of water, 90 ml of acetic acid, and 30 ml of concentrated sulfuric acid was refluxed until exothermic oxidation set in. When heat ceased to be evolved, the reaction mixture was boiled further for one hour. Cooling, filtering, and drying of the residue gave 1.90 g (39.2%) of terephthalic acid—the same yield of terephthalic acid as was obtained by oxidation under the same conditions of the corresponding mixture of chloromethylation products from toluene, i.e., a yield corresponding to a content of para isomer of 48.3%.

In oxidations under strictly identical conditions we obtained the following results.

b) From 2.0 g of the mixture of alcohols obtained by hydrolysis of the bromomethylation product from ethylbenzene, 15 g of chromium trioxide, 45 ml of water, 45 ml of acetic acid, and 15 ml of concentrated sulfuric acid, we obtained 1.55 g (63.4%) of terephthalic acid, which corresponds to 75.7% of para isomer. When the experiment was repeated, 1.53 g of terephthalic acid was obtained.

From 2.0 g of the mixture of alcohols obtained by hydrolysis of the chloromethylation product from ethylbenzene, we obtained 1.58 g (64.7%) of terephthalic acid, which corresponds to 77.3% of para isomer. In a repeat experiment we obtained 1.58 g of terephthalic acid.

c) From 2.20 g of the mixture of alcohols obtained by hydrolysis of the bromomethylation product from cumene, we obtained 1.79 g (73.6%) of terephthalic acid, which corresponds to 86.7% of para isomer. In a repeat experiment we obtained 1.77 g of terephthalic acid.

From 2.20 g of the mixture of alcohols obtained by hydrolysis of the chloromethylation product from cumene, we obtained 1.80 g (74.0%) of terephthalic acid, which corresponds to 87.2% of para isomer. In a repeat experiment we obtained 1.82 g of terephthalic acid.

Terephthalic acid was identified via its dimethyl ester, which was prepared by boiling it with methanol in presence of sulfuric acid. The ester melted at 141-142°, and there was no depression in admixture with a known sample.

### Oxidation of Bromomethylation Products of Aromatic Hydrocarbons with Dilute Nitric Acid at 200°

a) A mixture of 5.0 g of the mixture of (bromomethyl) toluenes and 90 ml of 10% nitric acid was prepared in a 200-ml rotating autoclave. The mixture was agitated at 200° for 90 minutes. The reaction mixture was cooled, and 1.73 g of terephthalic acid was filtered off. The mother liquor was evaporated down to small bulk and yielded 1.0 g of phthalic acid, which was recrystallized from 5% hydrochloric acid and boiled for 15 minutes with aniline, which gave the anilide, m.p. 205-207° after recrystallization from methanol; there was no depression in a mixture test with a known sample. Total yield of acids 60.9%.

In oxidations under analogous conditions we obtained the following results.

b) Reaction of 5.0 g of the mixture of (bromomethyl)ethylbenzenes with 90 ml of 10% nitric acid gave 2.5 g of terephthalic acid and 0.79 g of phthalic acid, which was converted into its anilide, m.p. 207-208°. Total yield of acids 80.5%.

c) Reaction of 5.0 g of the mixture of (bromomethyl) cumenes with 60 ml of 20% nitric acid gave 2.91

g of terephthalic acid and 0.12 g of phthalic acid. Total yield of acids 77.8%.

In all cases the terephthalic acid obtained was identified via its dimethyl ester, m.p. 141-142°, undepressed by admixture of a known sample.

#### SUMMARY

1. Bromomethylation of toluene, ethylbenzene, and cumene gave high yields (about 80%) of the corresponding mono(bromomethyl) derivatives in the form of a mixture of ortho and para isomers, the quantitative proportions of which were established by the method of oxidation into the corresponding benzenedicarboxylic acids.

2. It was shown that in the chloro- and bromo-methylation of these aromatic hydrocarbons under identical conditions, mixtures of mono(halomethyl) derivatives of the same composition are formed.

3. In the bromomethylation of toluene, ethylbenzene, and cumene the substituent has a steric effect on orientation in the reaction which is analogous to that observed in the chloromethylation of these hydrocarbons (as we pass from toluene to ethylbenzene and further to cumene, the relative amount of para isomer rises sharply).

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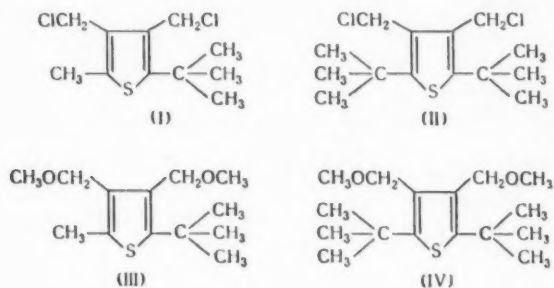
# ACTION OF RANEY NICKEL ON ETHERS OF THE THIOPHENE SERIES

Ya. L. Goldfarb and P. A. Konstantinov

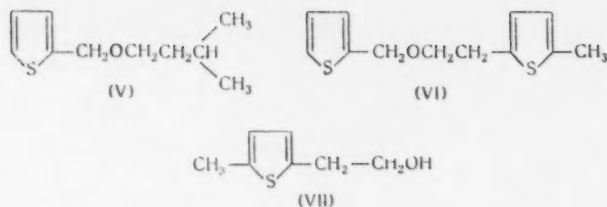
It has been shown in our laboratory and by various foreign workers that it is possible to prepare aliphatic compounds having one or two functional groups from thiophene and its homologs [1-5]. The method is based on the fact that, when thiophene derivatives are treated with Raney nickel, C-S linkages are more readily broken than C-C, C-N, C=O, and certain other linkages.

In this connection it was of interest to investigate the action of Raney nickel on thiophene compounds containing an ether grouping. On the basis of existing data on the behavior of aliphatic ethers toward Raney nickel, it could be expected that in ethers derived from thiophene, scission would occur preferentially at the C-S linkage under our conditions; this would open up a new route to the preparation of aliphatic ethers. Thus, in the work of van Duzee and Adkins [6] a considerable number of examples were brought forward to show that ethers are fairly stable toward Raney nickel, decomposition becoming evident only above 200°, when it proceeds most readily in the case of benzyl ethers.

The necessary ethers of the thiophene series were synthesized by the action of the corresponding alkoxides on chloromethyl derivatives of thiophene and its homologs.\* From 2-tert-butyl-5-methyl- and 2,5-di-tert-butyl-thiophenes, 2-tert-butyl-3,4-bis(chloromethyl)-5-methylthiophene (I) and 2,5-di-tert-butyl-3,4-bis(chloromethyl)thiophene (II) were prepared under the conditions described below. It must be mentioned that chloromethylation of these 2,5-dialkylthiophenes in the free  $\beta$ -positions proceeded without complications and the chloromethyl derivatives were obtained in comparatively high yields. By the action of sodium methoxide in excess of absolute methanol on the chloro compounds (I) and (II) we prepared 2-tert-butyl-3,4-bis(methoxymethyl)-5-methylthiophene (III) and 2,5-di-tert-butyl-3,4-bis(methoxymethyl)thiophene (IV) in yields attaining 80-95%. By the same method, starting from 2-(chloromethyl)thiophene and isopentyl alcohol, we synthesized the previously unknown isopentyl 2-thienyl ether (V).

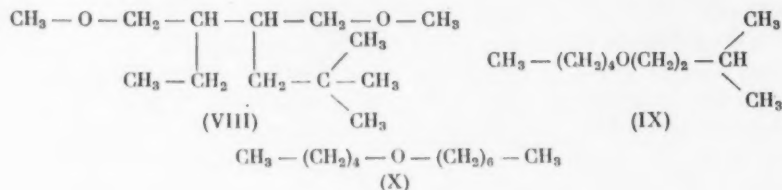


\* An ether of the thiophene series was first prepared by this method by Cairns and McKusick [7].

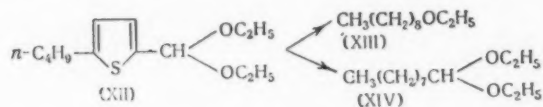


For the preparation of higher aliphatic ethers with fairly long carbon chains, considerable interest is presented by ethers in which both radicals are derived from thiophene. In this case it may be possible to make use of the aromatic character of not only one, but at least two thiophene nuclei. The alcohols required for this purpose may be synthesized from thiophene and its derivatives— for example, by the action of ethylene oxide on the appropriate organomagnesium or organolithium compounds [8]. We prepared one ether of this type (VI) by the condensation of 2-(chloromethyl) thiophene with 5-methyl-2-thiopheneethanol (VII). In this, as in previous cases, it was necessary to use excess of alcohol, since reduction of the amount used to that corresponding to equimolecular proportions resulted in a sharp drop in the yield of ether.

Investigation of the action of Raney nickel on the ethers listed above \* showed that in all cases except that in which the sulfur atom was screened by two *tert*-butyl groups [the ether (IV)] sulfur could be eliminated under very mild conditions (in a diethyl ether medium) and in a comparatively short period of time, sometimes not exceeding 15 minutes. By this method the ethers (III) and (V) gave, respectively, 4,5-bismethoxymethyl-2,2-dimethylheptane (VIII) and isopentyl pentyl ether (IX); from 2,5-di-*tert*-butyl-3,4-bismethoxymethylthiophene (IV), however, the corresponding open-chain ether could not be obtained even after a 17-hour boil. On the other hand, 2-(5-methyl-2-thienyl)ethyl thienyl ether (VD), which contains two thiophene nuclei, was decyclized without complications and gave heptyl pentyl ether (X).



In the light of these results it was considered to be of interest to investigate the action of Raney nickel on acetals of the thiophene series. These, although containing a hidden aldehyde function, formally contain two C—O—C linkages and in this sense may be included within the scope of our investigation. As starting materials we took diethyl acetals of 2-thiophenecarboxaldehyde (XI) and 5-butyl-2-thiophenecarboxaldehyde (XII). By the action of Raney nickel on the acetal (XII) we obtained a mixture of products distilling over a range of 16°. Fractionation of this mixture gave two fractions, of which the first was found to be ethyl monyl ether (XIII) in admixture with some nonanaldiethyl acetal (XIV), and the second consisted mainly of this acetal (XIV) together with a little of the ether (XIII).



\* Only one example of the hydrogenolysis of an ether of the thiophene series over Raney nickel has been reported in the literature [9].

Although the analytical results were not altogether satisfactory, it may be considered that the compounds composing these mixtures were those indicated above. The content of the acetal (XIV) in the second fraction, as determined by its precipitation in an acid medium as the 2,4-dinitrophenylhydrazone of nonanal (XV), attained 95-99%. The elementary analysis of the 2,4-dinitrophenylhydrazone corresponded to that required for (XV), but the melting point that we found was 7° higher than that reported in the literature [8]. The acetal (XI) gave the diethyl acetal of valeraldehyde (XVI), from which we prepared a 2,4-dinitrophenylhydrazone that corresponded in composition to the 2,4-dinitrophenylhydrazone of valeraldehyde, though in this case also the observed melting point was higher (by 10°) than that reported in the literature [11].

The results obtained in the investigation of the action of Raney nickel on these two acetals do not give a complete picture of the behavior to be found, but they lead us to expect that by observing certain conditions we may obtain various acetals, and therefore aliphatic aldehydes, from aldehydes of the thiophene series. We are continuing work in this direction.

#### EXPERIMENTAL

Isopentyl 2-Thenyl Ether (V): 2-(Chloromethyl)thiophene (20 g, i.e., 0.16 mole) was added dropwise over a period of 15-20 minutes to a stirred solution of 3.8 g (0.165 mole) of sodium in 75 ml of dry isopentyl alcohol. The mixture was then heated for three hours in a boiling water bath. The mixture was cooled, diluted with 150 ml of water, and extracted with ether. The ether layer was washed with water and dried over anhydrous magnesium sulfate. Ether and excess of isopentyl alcohol were distilled off, and fractionation at 16 mm then gave Fraction I, 0.3 g, b.p. up to 108°, Fraction II, 22.1 g, b.p. 109-110°, and a residue of 1.1 g.

Refractionation of Fraction II gave 21 g (77%) of the required ether, b.p. 112-113° (17 mm);  $n_D^{20}$  1.4920;  $d_4^{20}$  0.9908. Found MR 53.96, Calculated MR 54.15.

Found %: C 65.30, 65.07; H 8.37, 8.53  $C_{10}H_{16}OS$ . Calculated %: C 65.17; H 8.75

2-tert-Butyl-3,4-bis(chloromethyl)-5-methylthiophene (II). A strong current of hydrogen chloride was passed for 40 minutes into a mixture of 35 g of 36% formalin and 150 ml of glacial acetic acid. When the temperature had fallen to 43°, 16.5 g (0.11 mole) of 2-tert-butyl-5-methylthiophene was added gradually with vigorous stirring. To complete reaction, passage of hydrogen chloride and stirring was continued further for one hour. The reaction product was then poured into 500 ml of ice water and extracted with benzene. The extract was washed with water and dried with calcium chloride. Benzene was distilled off, and vacuum distillation of the residue at 7 mm gave Fraction I, 0.8 g, b.p. up to 140°, Fraction II, 18.2 g, b.p. 141-146°, and a residue of 2.8 g.

Refractionation of Fraction II gave 17.6g (67%) of a colorless, viscous substance, b.p. 137-139° (7 mm);  $n_D^{20}$  1.5515;  $d_4^{20}$  1.1895; Found MR 67.45; Calculated MR 66.96.

Found %: C 52.86, 53.04; H 6.56, 6.44  $C_{11}H_{16}SCl_2$ . Calculated %: C 52.60; H 6.41

2-tert-Butyl-3,4-bismethoxymethyl-5-methylthiophene (III). 2-tert-Butyl-3,4-bis(chloromethyl)-5-methylthiophene (16.5 g, i.e., 0.107 mole), prepared as indicated above, was added gradually to a solution of sodium methoxide prepared by dissolving 4 g (0.17 mole) of sodium in 60 ml of dry methanol. The mixture was boiled for three hours in a water bath and was left overnight. The mixture was then poured into 200 ml of water and extracted with ether. The extract was washed with water and dried over magnesium sulfate. Ether was distilled off, and distillation of the residue at 7 mm gave Fraction I, a few drops boiling up to 127°, Fraction II, 14.6 g, b.p. 128-130°, and a residue of 0.4 g. Refractionation of Fraction II gave 14 g (97%) of a colorless viscous liquid which boiled at the same temperature as before;  $n_D^{20}$  1.5070;  $d_4^{20}$  1.0253; Found MR 70.19; Calculated MR 69.65

Found %: C 64.16, 64.41; H 9.21, 9.26; S 13.07, 12.98  $C_{13}H_{22}OS$ . Calc. % C 64.42; H 9.15; S 13.22

2,5-Di-tert-butyl-3,4-bismethoxymethylthiophene (IV). This was obtained by mixing solutions of 5 g of sodium in 50 ml of absolute methanol and 18 g (0.06 mole) of 2,5-di-tert-butyl-3,4-bis(chloromethyl)thiophene



in 60 ml of absolute methanol and then boiling the mixture under reflux for four hours. After further treatment (see above), the product was vacuum-fractionated (7 mm): Fraction I, 0.1 g, b.p. up to 137°; Fraction II, 15.3 g, b.p. 137-142°; residue 0.9 g.

Refractionation of Fraction II gave 14.5 g (79%) of a colorless oil, b.p. 139-141° (6 mm);  $n_D^{20}$  1.5058;  $d_4^{20}$  1.0072; Found MR 83.68; Calculated MR 83.50

Found %: C 67.90, 68.01; H 9.98, 9.99; S 11.08, 11.25.  $C_{16}H_{28}O_2S$ . Calculated %: C 67.56; H 9.92; S 11.11.

5-Methyl-2-thiopheneethanol (VII). 2-Methylthiophene (49 g, i.e., 0.5 mole) was added with continuous stirring to butyllithium prepared from 12.5 g of lithium in 800 ml of absolute ether; the temperature of the mixture was maintained in the range 0-4°. The cooling bath was then removed, the mixture was warmed to 25°, and a solution of 24.2 g (0.55 mole) of ethylene oxide in 60 ml of dry ether was added dropwise. The mixture was poured into ice water and extracted with ether; the extract was washed with water and dried over magnesium sulfate. Ether was distilled off, and vacuum distillation of the residue at 19 mm gave Fraction I, 1.6 g, b.p. up to 119°, Fraction II, 49.8 g, b.p. 119-120°, and a residue of 1 g.

Refractionation of Fraction II gave 48.2 g (68%) of a colorless substance, b.p. 95-96° (7 mm);  $n_D^{20}$  1.5364;  $d_4^{20}$  1.0988; Found MR 40.41; Calculated MR 39.96.

Found %: C 58.96, 59.28; H 7.12, 7.31; S 22.16, 22.56.  $C_7H_{10}OS$ . Calculated %: C 59.12; H 7.08; S 22.54.

After two crystallizations from hexane, the 1-naphthylurethan (colorless needles) melted at 112.5-113.5°.

Found %: N 4.58, 4.41.  $C_{18}H_{17}O_2NS$ . Calculated %: N 4.49

2-(5-Methyl-2-thienyl)ethyl Thienyl Ether (VI). Sodium (3.7 g, i.e., 0.16 mole) was added to 47 g (0.33 mole) of 5-methyl-2-thiopheneethanol prepared as indicated above. In order to complete reaction the mixture was heated for two hours at 150-160° and was left until the next day. Dry toluene (50 ml) was added to the mixture, which was heated to 120° and stirred while 20 g (0.15 mole) of 2-(chloromethyl)thiophene was added dropwise over a period of one hour. Heating was then continued for two hours, and the mixture was set aside overnight. After further treatment the product was vacuum-fractionated (6 mm): Fraction I, 1.1 g, b.p. up to 90°; Fraction II, 21.5 g, b.p. 90-95° [the original alcohol (VII)]; Fraction III, 1.6 g, b.p. 96-155°; Fraction IV, 28.3 g, b.p. 156-157°; residue 3.6 g.

Refractionation of Fraction IV gave 27 g of substance of b.p. 139-140° (4 mm);  $n_D^{20}$  1.5710;  $d_4^{20}$  1.1563; Found MR 67.73; Calculated MR 67.51.

Found %: C 60.43, 60.34; H 6.02, 6.02; S 27.09, 26.60  $C_{12}H_{14}OS_2$ . Calculated %: C 60.46; H 5.91; S 26.90

2-Thiophenecarboxaldehyde Diethyl Acetal (XI). This was prepared by Arbuzov and Klaisen's method [12, 13]. Concentrated hydrochloric acid (one drop) was added to a mixture of 10.8 g (0.1 mole) of 2-thiophenecarboxaldehyde, 16.3 g (0.11 mole) of orthoformic ester, and 13.8 g of absolute ethanol. The temperature then rose to 28°. The mixture was refluxed for three hours and then cooled rapidly with ice water. Acid was neutralized with a few drops of 0.5 N alcoholic potassium hydroxide. Alcohol and ethyl formate were distilled off and the residue was distilled at ordinary pressure. A fraction (15.4 g) of b.p. 214-219° was collected, and a residue of 0.45 g remained. The product was redistilled at 14 mm: Fraction I, 0.4 g, b.p. up to 96°; Fraction II, 14.9 g, b.p. 96-98° and  $n_D^{20}$  1.4980, which is in accord with data cited by Grishkevich-Trokhimovsky [14].

5-Butyl-2-thiophenecarboxaldehyde Diethyl Acetal (XII). This was prepared by the above-described method from 11 g (0.35 mole) of 5-butyl-2-thiophenecarboxaldehyde. Vacuum fractionation of the reaction product gave: Fraction I, 1.2 g, b.p. up to 135°; Fraction II, 12 g, b.p. 114-116°; residue in flask, about 1 g.

Refractionation of Fraction II at 5 mm gave 11.4 g of the acetal, b.p. 109-110°;  $n_D^{20}$  1.4840; Found MR 69.72; Calculated MR 69.64.



Found %: C 64.88, 64.77; H 9.22, 9.23; S 12.87, 12.91,  $C_{13}H_{22}O_2S$ . Calculated %: C 64.44  
H 9.15; S 13.23

Isopentyl Pentyl Ether (IX). A mixture of 9 g (0.05 mole) of isopentyl 2-thenyl ether, 500 ml of diethyl ether, and 45 g of Raney nickel prepared by Adkins and Billica's method [15] was heated under reflux with stirring for 15 minutes, at the end of which time a test for sulfur was negative. The nickel was filtered off and washed several times with ether, the filtrate was dried over magnesium sulfate, ether was distilled off, and the residue was distilled at ordinary pressure: Fraction I, a few drops, b.p. 172°; Fraction II, 5.2 g, b.p. 173-195°; residue, 0.9 g.

Refractionation gave 4.7 g (61%) of the ether, b.p. 173-174.5°,  $n_D^{20}$  1.4190;  $d_4^{20}$  0.7860; Found MR 49.79; Calculated MR 50.02.

Found %: C 76.01, 75.91; H 14.01, 13.77,  $C_{10}H_{22}O$ . Calculated %: C 75.87; H 13.94

4,5-Bismethoxymethyl-2,2-dimethylheptane (VIII). This was prepared by heating a solution of 10 g (0.04 mole) of 2-tert-butyl-3,4-bismethoxymethyl-5-methylthiophene in 600 ml of ether with 50 g of Raney nickel. Desulfurization was complete in 90 minutes. Vacuum fractionation of the product (31 mm) gave: Fraction I, 0.15 g, b.p. up to 131°; Fraction II, 5.5 g, b.p. 134-137°; residue 0.9 g.

Refractionation of Fraction II over sodium gave 4.98 g (56%) of the ether, b.p. 123-125° (28 mm);  $n_D^{20}$  1.4111;  $d_4^{20}$  0.8711; Found MR 65.61; Calculated MR 65.50.

Found %: C 72.40; H 12.70,  $C_{13}H_{28}O_2$ . Calculated %: C 72.16; H 13.00

Heptyl Pentyl Ether (X). A solution of 10 g (0.04 mole) of 2-(5-methyl-2-thienyl)ethyl thienyl ether in 600 ml of diethyl ether was refluxed with 50 g of Raney nickel with stirring for eight hours. Distillation of the product at 40 mm gave: Fraction I, 0.4 g, b.p. up to 126°; Fraction II, 4.4 g, b.p. 126-128°; residue, 0.9 g.

Refractionation of Fraction II gave 3.9 g (50%) of the ether, b.p. 87-88° (10 mm);  $n_D^{20}$  1.4200;  $d_4^{20}$  0.7965; Found MR 59.20; Calculated MR 59.26.

Found %: C 77.31, 77.10; H 13.93, 13.95,  $C_{12}H_{26}O$ . Calculated %: C 77.34; H 14.06

Valeraldehyde Diethyl Acetal (XVI). A solution of 9 g (0.05 mole) of 2-thiophenecarboxaldehyde diethyl acetal in 500 ml of diethyl ether was refluxed with 45 g of Raney nickel for eight hours. Every two hours a qualitative test for sulfur was made, toward the end of the eight hours it became negative. The catalyst was filtered off and washed with ether, and the filtrate was dried over magnesium sulfate. Ether was distilled off, and distillation of the residue at ordinary pressure gave: Fraction I, 0.9 g, b.p. 115-161°; Fraction II, 4.9 g, b.p. 162-166°; residue, 1 g.

Refractionation of Fraction II gave 3.8 g (50%) of valeraldehyde diethyl acetal, b.p. 162.5-163.5;  $n_D^{20}$  1.4021;  $d_4^{20}$  0.8304; Found MR 47.00; Calculated MR 47.05.

Found %: C 67.57; 67.55; H 12.38, 12.66,  $C_9H_{22}O_2$ . Calculated %: C 67.45; H 12.58

According to the literature [16], the diethyl acetal (XVI) has been obtained in 48% yield from butylmagnesium bromide and ethyl orthoformate.

2,4-Dinitrophenylhydrazone of Valeraldehyde. This was prepared by adding 0.4 g of the acetal (XVI) to a solution of 1 g of 2,4-dinitrophenylhydrazine in 40 ml of 2 N HCl. The mixture rapidly became turbid and a precipitate of the 2,4-dinitrophenylhydrazone of valeraldehyde formed. It was filtered off and washed with 2 N HCl and with water; after two crystallizations from alcohol and petroleum ether it melted at 107-108° (the literature [11] gives 98°).

Found %: N 21.17; 20.88 Calculated %: N 21.04

Action of Raney Nickel on 5-Butyl-2-thiophenecarboxaldehyde Diethyl Acetal. A mixture of 9 g of the acetal, 500 ml of diethyl ether, and 45 g of Raney nickel was refluxed for three hours. Nickel was filtered off and washed with ether. Ether was distilled off, and distillation of the residue at 10 mm gave 4.7 g of pro-

duct, b.p. 92-108°. Fractionation gave: Fraction I, 0.87 g, b.p. 92-97°; Fraction II, 0.3 g, b.p. 98-105°; Fraction III, 3.03 g, b.p. 105-108°.

Analysis showed that Fraction I was close in composition to ethyl nonyl ether.

Found %: C 76.15; 76.11; H 13.09; 14.14  $C_{11}H_{24}O$ . Calculated %: C 76.74 H 13.95

The analysis of Fraction III corresponded to nonanal diethyl acetal.

Found %: C 72.64; 72.84; H 13.00; 12.86  $C_{13}H_{28}O_2$ . Calculated %: C 72.12; H 13.04

A little of Fraction III was converted into its 2,4-dinitrophenylhydrazone, m.p. 106-106.5° after three crystallizations from alcohol (the literature [10] gives m.p. 100°).

Found %: N 17.40; 17.38  $C_{15}H_{22}N_4O_4$ . Calculated %: N 17.38

#### SUMMARY

1. By the action of sodium alkoxides on chloromethyl derivatives of thiophene and its homologs, the following ethers were prepared: isopentyl 2-thenyl ether, 2-tert-butyl-3,4-bismethoxymethyl-5-methylthiophene, 2-(5-methyl-2-thienyl)ethyl thenyl ether, 2,5-di-tert-butyl-3,4-bismethoxymethylthiophene.

2. It was shown that Raney nickel reacts with ethers of the thiophene series with splitting of the C-S link and formation of aliphatic ethers.

3. The following ethers were obtained: isopentyl pentyl ether, heptyl pentyl ether, and 4,5-bismethoxymethyl-2,2-dimethylheptane.

4. Preliminary experiments on the action of Raney nickel on acetals of the thiophene series enables us to conclude that it is possible to retain the acetal grouping while eliminating sulfur.

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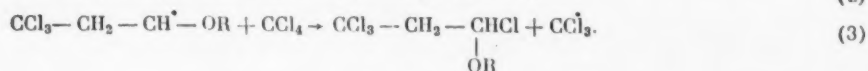
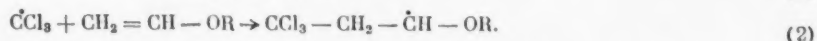
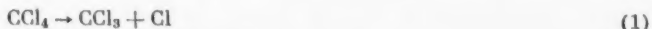
OLIGOMERIZATION  
COMMUNICATION 2. REACTION OF SOME VINYL ETHERS  
WITH CARBON TETRACHLORIDE IN PRESENCE OF  
VARIOUS INITIATORS

A. V. Bogdanova and M. F. Shostakovsky

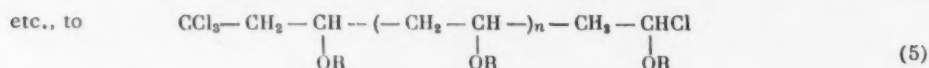
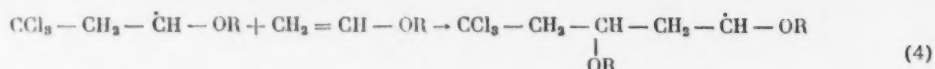
This paper describes the continuation of an investigation of the conditions under which vinyl ethers react with carbon tetrachloride. It has been reported [1] that butyl vinyl and ethyl vinyl ethers react with carbon tetrachloride in presence of benzoyl peroxide with formation of 1,3,3,3-tetrachloropropyl ethers. In the preceding communication [2] we described the extension of this reaction to aryl vinyl ethers and indicated the conditions for the formation of polymeric products in the addition of carbon tetrachloride to vinyl ethers in presence of benzoyl peroxide.

We were interested in the effect of other means of bringing about radical-induced changes on this reaction and also in the comparative study of the activities of various vinyl ethers in this process and their dependence on the nature of the initiator. Apart from benzoyl peroxide which activates vinyl ethers, 2,2'-azobis[2-methylpropionitrile] is well known as an initiator for polymerization reactions [3, 4] and for addition reactions of hydrogen sulfide [5], but these reactions either give low yields or require heating of the reaction mixture for many hours. In the reaction being studied, the effect of the dinitrile has been examined in one case only — formation of the product of equimolecular addition [6, 7]. Other means of free-radical initiation of reactions of polyhalomethanes have been tried only for the case of olefins. It is known, for example, that reaction between carbon tetrabromide and olefins can be initiated by irradiation [8, 9]. In studying these reactions with various olefins, the authors [9] found that reaction of styrene with carbon tetrabromide can be brought about by visible radiation, whereas addition of carbon tetrachloride with olefins requires ultraviolet radiation. In both cases both monomeric addition products and polymeric products were isolated. It is known also that platinized charcoal can be used as an activator of the radical-induced reaction of silicon tetrachloride with butadiene [10], the product being 2-butenyltrichlorosilane.

The present paper describes an investigation of the effect of temperature, ultraviolet radiation, 2,2'-azobis[2-methylpropionitrile], and platinum on the reaction of vinyl ethers with carbon tetrachloride, and also a study of the conditions for the decomposition of 1,3,3,3-tetrachloropropyl ethers and the products obtained. Reactions of vinyl ethers in presence of these initiators result in the formation of both simple addition products and polymeric products; they are free-radical chain reactions. The course of these reactions can be represented in the form of schemes similar to those describing the reaction of olefins with polyhalomethanes [11, 12]. First of all, under the influence of the initiator, carbon tetrachloride forms a free radical, which brings about a further transformation:

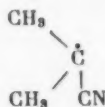


Formation of the polymeric product may proceed by the reactions:

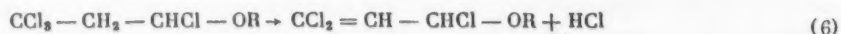


Study of the conditions for reaction of vinyl ethers with carbon tetrachloride showed that alkyl vinyl and cyclohexyl vinyl ethers react with carbon tetrachloride under the influence of heat with formation of simple addition products or of polymeric products, depending on the relative amounts of reactants taken. For example, butyl vinyl ether and carbon tetrachloride, which were purified from traces of peroxy compounds just before the experiment, were sealed in a tube through which oxygen-free nitrogen had been passed for 20 minutes. The tube was heated at 90° for three hours, and distillation of the reaction mixture then gave butyl 1,3,3,3-tetrachloropropyl ether (26% yield) and a polymeric product containing chlorine. The use of the dinitrile and platinized charcoal, and also of ultraviolet radiation in conjunction with heating, considerably increased the yield of products.

When distilled, cyclohexyl 1,3,3,3-tetrachloropropyl ether decomposed with formation of hydrogen chloride, cyclohexyl 1,3,3-trichloroallyl ether, and sometimes 3,3-dichloroacrolein dicyclohexyl acetal. These products always accompanied the formation of cyclohexyl 1,3,3,3-tetrachloropropyl ether. The polymeric products obtained from vinyl ethers and carbon tetrachloride were similar to the polymers obtained in presence of ultraviolet radiation or of benzoyl peroxide. They all contained chlorine, but no nitrogen, thus differing from poly[phenyl vinyl ether] [3] and poly[cyclohexyl vinyl ether] [4] prepared in presence of the dinitrile and containing an initiator residue in the molecule. In these reactions benzoyl peroxide and the dinitrile cause the formation of the  $\text{CCl}_3$  radical, which initiates polymerization. In absence of carbon tetrachloride, polymerization in presence of, for example, the dinitrile begins with addition of the dinitrile radical to the double bond of the vinyl ether, this radical being



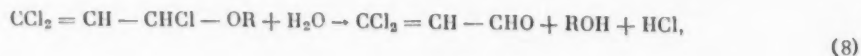
Tetrachloropropyl and trichloroallyl ethers, which are stable to storage in absence of moisture, decompose when heated with elimination of HCl:



and under more severe conditions:



Like tetrachloropropyl ethers [3], trichloroallyl ethers undergo hydrolysis with formation of dichloroacrolein in good yield:



Butyl tetrachloropropyl ether decomposes readily and, depending on the temperature, gives products of different degrees of degradation (Equations 6 and 7). Phenyl tetrachloropropyl ether decomposes smoothly at 160-170° with formation of the trichloroallyl ether; under more severe conditions decomposition proceeds further and the dichloroacrolein formed appears to give condensation products with the phenol residue.

## EXPERIMENTAL

### 1. Reaction of Butyl Vinyl, Cyclohexyl Vinyl, and Phenyl Vinyl Ethers with Carbon Tetrachloride in presence of Various Initiators

A weighed amount (10-60 g) of the vinyl ether and the amount of carbon tetrachloride corresponding to the selected ratio of components were placed in a three-necked flask fitted with stirrer, thermometer, and reflux condenser. If reaction was to be carried out in presence of an initiator, a weighed amount of this was now introduced (0.5% of platinized charcoal (2% Pt) or 2% of 2,2'-azobis[2-methylpropionitrile] on the weight of the ether). If reaction was to be carried out in presence of ultraviolet radiation, the reaction flask was irradiated with a quartz lamp during the whole reaction period. The mixture was stirred while the flask was heated in an oil bath to 85-90°, at which temperature reaction generally set in and continued for three hours. The flask was cooled and the reaction mixture was filtered if platinum had been used. Excess of carbon tetrachloride or vinyl ether was distilled off, and the residue was vacuum-fractionated. When the reaction was carried out in sealed tubes, the reactants were sealed in the tube, which was placed in a protective metal tube and heated in a water bath for three hours.

The results of the most characteristic experiments are given in Table 1. The products isolated had constants which agreed with values previously reported (Table 2).

A polymer— a product of the addition of carbon tetrachloride to the vinyl ether— was isolated from the undistillable residue or from the crude product by reprecipitation [2]. It was dried in a vacuum desiccator and analyzed.

The polymeric addition product obtained from butyl vinyl ether and carbon tetrachloride in a sealed tube had the following composition: C 68.98, 68.83%; H 11.42, 11.51%; Cl 2.73, 2.79%. This polymer is close in composition to that obtained previously [2] in presence of benzoyl peroxide and contains about 40 molecules of butyl vinyl ether per molecule of CCl<sub>4</sub>.

### 2. Thermal Decomposition of 1,3,3,3-Tetrachloropropyl Ethers

1) Decomposition of Phenyl 1,3,3,3-Tetrachloropropyl Ether. Freshly distilled phenyl 1,3,3,3-tetrachloropropyl ether (35 g) was heated in a feeble current of dry nitrogen in a flask fitted with a fractionation column attached to a condenser. The condenser was connected to a coil trap cooled with ice and two Ivitsky vessels containing distilled water to absorb hydrogen chloride. The flask was heated in Wood's metal, the temperature of which was maintained at 160-170° for four hours. The dark-colored product was vacuum-fractionated:

Fraction I B.p. 100-107° (2 mm);	25.5 g
Fraction II B.p. 107-110° (2 mm);	6.8 g
Residue	0.7 g

After two distillations Fraction I had the following constants: b.p. 97-97.5° (1 mm);  $n_D^{20}$  1.5500;  $d_4^{20}$  1.3647; Found MR 55.43; Calculated for C<sub>9</sub>H<sub>7</sub>OCl<sub>3</sub>F<sub>4</sub> MR 55.94. It consisted of phenyl 1,3,3-trichloroallyl ether, obtained in 84% yield.

Found %: C 44.26, 44.35; H 2.95, 2.96; Cl 45.10, 45.30. C<sub>9</sub>H<sub>7</sub>OCl<sub>3</sub>. Calculated %: C 45.48; H 2.97; Cl 44.75

Fraction II was phenyl 1,3,3,3-tetrachloropropyl ether, b.p. 109-110° (2 mm);  $n_D^{20}$  1.5432.

Heating of 10 g of phenyl 1,3,3,3-tetrachloropropyl ether at 200° for four hours gave 2.5 g of hydrogen chloride and 7.1 g of resinous residue, which contained chlorine and was insoluble in the usual organic solvents.

2) Decomposition of Butyl 1,3,3,3-Tetrachloropropyl Ether and of Ethyl 1,3,3,3-Tetrachloropropyl Ether. The thermal decomposition of these ethers was carried out under the above-described conditions. Table 3 gives



TABLE 1

Experiment No.	Original vinyl ether	Molar ratio ether:CCl <sub>4</sub>	Initiator	Reaction temperature (°C)	Yields of products	
					1,3,3,3-tetrachloropropyl ether (%)	Polymeric-addition product (% on original mixture)
1	Butyl vinyl ether	1:3	—	92	26.4	3.0
2		1:6	—	82	50.0	1.4
3		6:1	—	90 in sealed tube	—	89.0
4		1:3	Ultraviolet radiation	82	87.3	2.5
5	Cyclohexyl vinyl ether	1:3	Dinitrile	92	90.6	2.3
6		6:1	"	95	—	42.7*
7		1:3	Pt on charcoal	82	94.5	2.0
8		1:3	—	90	21.4	14.1**
9		6:1	—	85	—	18.0
10		1:3	Ultraviolet radiation	90	—	—
11	Phenyl vinyl ether	1:3	Dinitrile	85	54.0	5.1***
12		6:1	"	80	—	53.3
13		1:3	Pt on charcoal	86	32.5	5.8****
14		1:3	Ultraviolet radiation	93	66.4	2.7
15		6:1	"	115	13.6	8.0
16		1:3	Dinitrile	93	87.0	3.7
17		6:1	"	90 in sealed tube	—	16.4*****

\* Also isolated: 24.8% of butyl vinyl ether and 9.3% of trichloropropionaldehyde dibutyl acetal.

\*\* Also isolated: 8% of cyclohexyl vinyl ether and 16% of dichloroacrolein dicyclohexyl acetal.

\*\*\* 16% of cyclohexyl vinyl ether was recovered unchanged.

\*\*\*\* Also isolated: 4.6% of the vinyl ether and 30% of dichloroacrolein dicyclohexyl acetal.

\*\*\*\*\* 69% of phenyl vinyl ether was recovered unchanged.

TABLE 2

Ether	B.p. in °C (p in mm)	$n_D^{20}$	$d_4^{20}$	Literature references
Butyl 1,3,3,3-tetrachloropropyl	73.5—74 (1)	1.4690	1.2615	[1,2]
Cyclohexyl 1,3,3,3-tetrachloropropyl	111—112° (2)	1.5000	1.2405	[13]
Phenyl 1,3,3,3-tetrachloropropyl	146—147° (12)	1.5430	1.3969	[2]

results on the decomposition of butyl tetrachloropropyl ether at different temperatures.

Constants of isolated decomposition products: butyl 1,3,3-trichloroallyl ether: b.p. 117–118° (22 mm);  $n_D^{20}$  1.4735;  $d_4^{20}$  1.2102; Found MR 50.48; Calculated for  $C_7H_{11}OCl_3$  MR 50.30 (the literature [1] gives b.p. 97–98° (11 mm);  $n_D^{17.5}$  1.475;  $d_4^{17.5}$  1.217. 3,3-Dichloroacrolein: b.p. 57° (49 mm);  $n_D^{20}$  1.5050;  $d_4^{20}$  1.4277; Found MR 25.95; Calculated for  $C_3H_2OCl_2$  MR 25.24. (the literature [1, 7] gives b.p. 124–125°;  $n_D^{20}$  1.5067). The 2,4-dinitrophenylhydrazone of the dichloroacrolein melted at 163°. Butyl chloride: b.p. 77.5–78°  $n_D^{20}$  1.4025;  $d_4^{20}$  0.8975. The residue contained 11.5% of chlorine.



TABLE 3

Decomposition temperature (°C)	Yield (%)			Resinous residue (yield in % original ether)
	Butyl 1,3,3-trichloroallyl ether	C <sub>4</sub> H <sub>7</sub> Cl	3,3-Dichloroacrolein	
130—135	89.7	8.2	—	1.2
200—230	16.0	50.2	29.6	13.5

Ethyl tetrachloropropyl ether decomposed similarly when heated. The ethyl 1,3,3-trichloroallyl ether isolated had the following constants: b.p. 42.6–42.8° (31 mm);  $n_D^{20}$  1.5060;  $d_4^{20}$  1.3982; Found MR 40.36. Calculated for C<sub>5</sub>H<sub>6</sub>OC1<sub>3</sub> MR 41.07.

Found %: Cl 56.00; 56.26 C<sub>5</sub>H<sub>7</sub>OC1<sub>3</sub>. Calculated %: Cl 56.15

3) Hydrolysis of Ethyl 1,3,3-Trichloroallyl Ether. A mixture of 1.4 g of ethyl 1,3,3-trichloroallyl ether and 15 ml of water was refluxed for one hour. From the hydrolyzate 1.2 g (92%) of the semicarbazone of 3,3-dichloroacrolein was isolated. After being recrystallized from boiling alcohol, the semicarbazone melted at 166.5° in a sealed capillary and had the following elementary composition:

Found %: C 26.52; 26.48; H 2.88; 2.83 C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>Cl<sub>2</sub>O. Calculated %: C 26.39; H 2.77

#### SUMMARY

1. An investigation was made of the reaction of vinyl ethers with carbon tetrachloride in presence of various agents capable of initiating reaction by a free-radical mechanism.

2. It was shown that platinized charcoal, 2,2'-azobis[2-methylpropionitrile], and also heating and ultra-violet irradiation, are good initiators for the formation of simple addition products and polymers from vinyl ethers and carbon tetrachloride. The reactions are rapid, and good yields are obtained.

3. Unlike other vinyl ethers investigated, phenyl vinyl ether does not react with carbon tetrachloride under the action of heat and in presence of platinum.

4. Study of the thermal decomposition of 1,3,3,3-tetrachloropropyl ethers showed that a 3-chloro is first eliminated as HCl and the resulting 1,3,3-trichloroallyl ether decomposes with elimination of alkyl halide, their behavior being like that of alkyl 1-chloroethyl ethers. In this respect the phenyl ether shows the same peculiarities as 1-chloroethyl phenyl ether does.

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## BRIEF COMMUNICATIONS

### ENERGY OF ADSORPTION FORCES AND HEAT OF ADSORPTION OF SIMPLE MOLECULES ON GRAPHITE

N. N. Avgul and A. V. Kiselev

Reliable calorimetric data have recently been published on heats of adsorption  $Q_{\alpha}$  on graphitized carbons for various molecules of simple structure: A [1], Kr [2],  $N_2$  [3], and  $NH_3$  [4]. Also, more precise values of the van der Waals radii  $r_B$  have been obtained for the same molecules [5]. In connection with our investigations on the calculation of adsorption energies of complex hydrocarbon molecules and comparison of these with calorimetric data on heats of adsorption [6, 7], it was considered to be of interest to calculate adsorption energies for these substances also and to compare the results with calorimetric data.

Adsorption energies of argon and nitrogen on graphite were calculated by Barrer [8], who determined the attraction constant  $C$  by Kirkwood's formula [9] and the distance between the argon or nitrogen molecule and the graphite  $r_0$  in the form of the sum of the  $r_B$  values and one half of the interplanar distance in graphite (1.7 Å). Barrer carried out the summation of the interactions of an adsorbate atom with the hundred nearest carbon atoms of the external plane of the graphite; he made the calculation for three different positions of the adsorbate molecule: 1) above the center of a hexagon of carbon atoms, 2) above a carbon atom, and 3) above the space between two adjacent carbons. Calculation showed that the first position is the most favorable. It is natural to expect that, when adsorbed, atoms or small simple molecules will preferentially occupy this energetically most favorable position.

Barrer assumed that  $r_B = 2.0$  Å for argon and nitrogen, and this has been shown to be too high [5].

In our paper [6], in calculating adsorption energies for complex hydrocarbon molecules on graphite, for each repeating unit  $i$  we carried out the summation of energies of interaction with the hundred nearest atoms of a space in the graphite lattice situated within a distance of less than  $r' = 8.5$  Å and integrated over the remaining volume of the lattice, so that

$$\Phi_i = -C_i \left[ \Sigma \left( \frac{1}{r^6} - \frac{1}{2} \frac{r_{0i}^6}{r^{12}} \right) + \frac{\pi \nu}{6 (r')^3} \right] = -C_i f(r, r_{0i}),$$

in which  $\nu$  is the number of carbon atoms in 1 cc of graphite. The values that we took for the van der Waals radius  $r_B$ , the polarizability  $\alpha$ , and the magnetic susceptibility  $\chi$  of the adsorbates are shown in the table. The corresponding values for graphite were given in the paper [8].

The calculation was carried out as follows. In the paper [6] we determined the relation between  $f(r, r_0)$  and  $r_0$  for the position of the adsorbed atom over a carbon atom. It follows from the graph for this relationship that for  $r_0 = 3.61$  Å,  $f(r, r_0)$  is  $2.93 \cdot 10^{45} \text{ cm}^{-6}$ . Transition to the more favorable position over the center of the hexagon increases the energy of interaction at  $r_0 = 3.7$  Å by 18%, according to Barrer [8]. Assuming that for the new value of  $r_0 = 3.61$  Å the same relationship holds, we obtained  $3.46 \cdot 10^{45} \text{ cm}^{-6}$  for  $f(r, r_0)$ . Values of  $f(r, r_0)$  were calculated similarly for the adsorption of other substances.

TABLE

Comparison of Results of Calculations of Energies of Dispersion and Repulsive Forces  $\Phi$  and Initial Differential Heats of Adsorption  $Q_{\alpha=0}$

Adsorbate	$r_D$ Å	$r_0$ Å	$f(r, r_0) \times 10^{-13}$ $\times 10^{-13}$	$-Z \times 10^{23}$ $\text{cm}^3$	$\pi \times 10^{24}$ $\text{cm}^3$	$C \times 10^{18}$ (kcal · cm <sup>6</sup> ) mole	$-\Phi$ kcal/mole	$Q_{\alpha=0}$ kcal/mole
Argon	1.91	3.61	3.46	32.2	1.63	0.77	2.6	2.6
Krypton	2.01	3.71	3.12	46.5	2.48	1.15	3.6	3.9
Nitrogen	1.75	3.45	3.97	19.9	1.76	0.65	2.6	2.7
Ammonia	1.69	3.39	4.25	27.4	2.26	0.87	3.7	6.2

Results of the calculations of values of  $f(r, r_0)$ ,  $C$  and  $\Phi$  are given in the table, which contains also experimental data for the differential heat of adsorption corresponding to the commencement of the formation of a monolayer on a homogeneous graphite surface  $Q_{\alpha=0}$ . On the graphitized carbons for which calorimetric measurements have been carried out, there usually remains a small proportion of heterogeneous places, so that in the initial stage of adsorption  $Q_{\alpha}$  showed a fall. When the heterogeneous places on the surface were filled, the heat of adsorption became almost constant and with further increase in the extent of filling the monolayer, it began to rise. This rise in  $Q_{\alpha}$  is associated with mutual attraction of adsorbate molecules in the adsorption layer. In order to determine the initial heat of adsorption on a homogeneous surface, as in the case of adsorption of hydrocarbons [6, 7] we extrapolated the middle part of the  $Q_{\alpha}-\alpha$  curve to  $\alpha=0$ , since this part of the curve corresponds to adsorption on the homogeneous part of the surface.\*

It will be seen from the table that, for the adsorption of A, Kr, and  $N_2$ , the theoretically calculated value of  $\Phi$  is in good agreement with the experimental value of  $Q_{\alpha=0}$ . \*\*

Much interest is presented by the case of adsorption of polar ammonia molecules on graphite. According to calorimetric data in the paper [4],  $Q_{\alpha=0}=6.2$  kcal/mole. Following the scheme indicated above, we calculated the energy of dispersion and repulsive interaction for ammonia and obtained 3.7 kcal/mole, which, unlike the values for nonpolar molecules, is considerably less than  $Q_{\alpha=0}$ .

In this case it is necessary to take account also of induction interaction between the ammonia dipole and carbon atoms of the graphite lattice. This problem has not been solved in detail except for cases of adsorption of polar molecules on metals for which interaction was calculated by the method of the mirror image of the dipole in the metal. As we treat graphite as a homopolar lattice [6, 8] and correspondingly calculate the adsorption potential with the aid of quantum-mechanical calculation of dispersion interactions, we can hardly justify the application of the simple mirror image method in this case, although Jaquet [13] applied this method to adsorption, even for the case of silica gel. Before developing a more rigorous method, which must take account of induction interaction of an adsorbate dipole with each of the neighboring atoms of the adsorbent lattice, we considered that it would be possible to make an approximate estimate by Jaquet's method of the contribution made to the adsorption energy by induction interaction. In the case of ammonia ( $\mu = 1.49$  D), calculation by Jaquet's formula gave 1.8 kcal/mole for low temperatures and 1.2 kcal/mole for high temperatures.

\* This follows from the results of the investigation [1], in which the heat of adsorption of argon was studied for a series of carbon blacks submitted to gradual graphitization. As the extent of graphitization increased, the initial steep fall on the curve for the differential heat of adsorption became less marked, but extrapolation of any of the  $Q_{\alpha}-\alpha$  curves for graphitized carbons to  $\alpha=0$  gave identical values of  $Q_{\alpha=0}$  of 2.6 kcal/mole.

\*\* After Barrer's work, energies of adsorption on graphite were calculated for argon in [10] (1.9 kcal/mole) and [11] (1.74 kcal/mole) and for krypton in [12] (2.8 kcal/mole). These calculations are in close accord with calorimetric experiments.

Hence, this approximate estimate indicates that the supplementary energy of the induction interaction of the ammonia dipole with graphite probably forms about one half of the energy of dispersion and repulsive interactions. Taking account of the energy of dispersion, attractive forces, and repulsive forces, which is equal — according to our calculation — to 3.7 kcal/mole for ammonia, we find it possible to explain satisfactorily the experimentally observed value of  $Q\alpha_0 = 6.2$  kcal/mole.

It is essential that these calculations, which we began in previous investigations [6, 7] for dispersion interactions of the nonpolar molecules of hydrocarbons, and more refined calculations of induction interactions for such polar molecules as those of ammonia, water, and hydrogen halides, should be developed further so that we may calculate the adsorption energies of the complex molecules of alcohols, amines, halogen derivatives, polar hydrocarbons, etc., in the adsorption of which various kinds of interaction with the graphite lattice are concerned.

#### SUMMARY

Adsorption energies of isolated atoms and simple nonpolar molecules on graphite were calculated on the basis solely of electric, magnetic, and geometric properties. The results of the theoretical calculation are in good agreement with experimental calorimetric data.

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10

# DEBYE DISPERSION OF ADSORBED WATER AT LOW TEMPERATURES

I. V. Zhilenkov

In the earlier stages of investigation the application of the dielectric method to the study of the physical properties of an adsorbed substance was confined to the determination of the relation between the dielectric permeability (DP) of the adsorbent-adsorbate system and the values of adsorption and temperature [1, 2]. At these stages of investigation, the choice of the frequency of the field acting on the dielectric during the measurements was largely arbitrary. Several investigations [3-8] have now been published in which studies are made of the dispersion of the complex DP of the adsorbent-adsorbate system with variation not only of temperature, but also of field frequency. It was shown that, depending on the ranges of temperature and frequency, we may observe dispersion due to the heterogeneity of the system or true Debye dispersion in the adsorbed substance.

Owing to this circumstance, we turned our attention to the fact that in the study of a substance in the adsorbed state, in the way that this was done in the first stage of investigation, the choice of field frequency may have a substantial effect on the results of the measurements. It is clear that, in the experimental study of the relation between DP and adsorption at a given temperature, it is necessary to be sure that the DP values used are free from the effect of frequency; that is to say, that we are dealing with static DP. Such DP values can be obtained from experimental data on dielectric dispersion. Only under these conditions can the dielectric isotherm serve as a basis for estimating the polarization of the adsorbate.

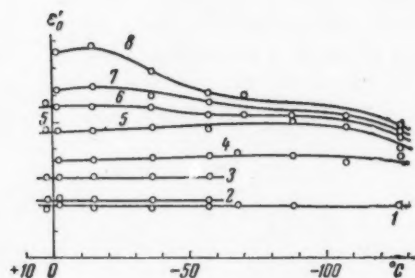


Fig. 1. Adsorption of water on K-2 silica gel (mmoles/g): 1)  $a = 0$ ; 2)  $a = 0.56$ ; 3)  $a = 2.77$ ; 4)  $a = 5.06$ ; 5)  $a = 10.8$ ; 6)  $a = 16.14$ ; 7)  $a = 21.1$ ; 8)  $a = 52.2$ .

Fig. 1. Before the measurements the silica gel was subjected to a vacuum at  $200^\circ$  for a long time. During the measurements, in order to increase thermal conductivity and to prevent distillation of the adsorbed water onto the cold walls, the condenser was filled with helium. An adsorption of 5.06 mmoles/g corresponded to a unimolecular layer.

As can be seen from Fig. 1, the temperature coefficient of the static DP of adsorbed water at low temperatures is almost zero. The same effect at positive temperatures was established by Kurbatov (at one arbitrary frequency) and explained on the assumption of limited rotation of the dipoles of the adsorbate. Also, polarization is great in the region of low adsorption, and the DP of the adsorbed substance is close to that of the substance in the normal liquid state.

Accordingly, we carried out measurements of complex DP for the adsorption of water on various silica gels as a function of temperature and extent of adsorption for frequencies ranging from 100 cycles per second to 10 megacycles per second. From dispersion curves obtained this way — in some cases directly and in others by extrapolation by the method of Cole and Cole [9] — we found the static DP values of the system. For finely porous K-2 silica gel with a surface of about 700 sq.m/g, total volume of pores of 0.72 cc/g, and probable pore diameter of 44 Å, the dependence of static DP on temperature and adsorption is shown in

This fact can scarcely be explained by limited rotation of adsorbed dipoles. As will be seen from Fig. 1, considerable temperature-dependence appears at a value of the adsorption  $\underline{a}$  corresponding to capillary condensation in this silica gel. For example, Curve 8 shows that at a temperature of  $-15$  to  $-20^\circ$  the DP of the adsorbed layer increases in the way found for the static DP of ordinary ice, which has been measured down to  $-60^\circ$  [10]. But whereas for ordinary ice the increase in static DP continues down to  $-60^\circ$  (no measurements have been carried out at lower temperatures) for water in the adsorbed layer a lowering of DP is observed in the range  $-15^\circ$  to  $-80^\circ$ , and a further lowering is observed below  $-100^\circ$ . It is probable that with lowering of temperature there is a change in the structure of the adsorbed layer with gradual elimination of degrees of freedom of adsorbed dipoles. The temperature of  $-15$  to  $-20^\circ$  is characteristic for capillary-condensation layers, and a temperature of  $-100^\circ$  for all layers, with the exception, possibly, of the first layer, for which it is still lower. In general features the phenomena observed for coarsely porous KSK-2 silica gel were similar.

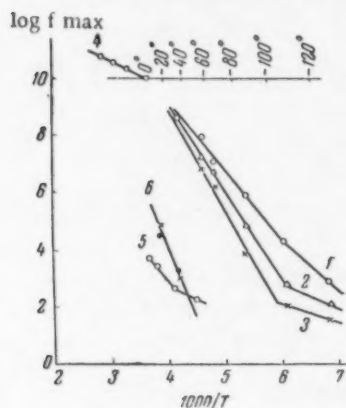


Fig. 2. Adsorption of water on K-2 silica gel: 1)  $\underline{a} = 5$ ; 2)  $\underline{a} = 20.3$ ; 3)  $\underline{a} = 50$ ; 4) liquid water; 5) ice; 6) adsorbed water in low-frequency region for  $\underline{a} = 20-50$  mmoles/g.

When, with the aid of the data of Fig. 1, we construct the graph of the relation between  $\epsilon''_0$  and  $\underline{a}$  at constant temperature (the dielectric isotherm), it is found that a linear relationship holds only for 1-2 monolayers, and with further increase in  $\underline{a}$  the rate at which  $\epsilon''_0$  increases falls. A convex dielectric isotherm is always obtained. Analysis of this relationship based on the theory of heterogeneous dielectrics shows that, if the structure of the system remains unchanged, the isotherm should be concave, and only when there is a transition from a structure of lamellar inclusions to one having inclusions of three-dimensional form can the dielectric isotherm have a convex form. The possibility cannot be excluded that the geometric structure of the adsorption layer does change in this way as we pass gradually from adsorption to capillary condensation.

Measurement of complex DP at various frequencies and temperatures makes it possible to find a constant time for the polarization process or for the electroconductivity process of adsorbed dipoles. In view of the dependence of the polarization of the adsorbed layer on temperature, discussed above, in the study of Debye dispersion we must prefer the frequency-variation method to the method of temperature variation. By the frequency-variation method we found the frequencies of relaxation maxima of coefficients of dielectric loss ( $\epsilon''$ )

TABLE

Substance	Temperature range ( $^\circ\text{C}$ )	Process	Activation energy (kcal/mole)	Order of frequency factor
Ice	0 to $-30$	Polarization	11,4	$10^{13}$
Ice	below $-30$	"	5,3	$10^8$
Ice	above $-50$	Conductivity	21,0	—
Water	above 0	Polarization	4,0	$10^{13}$
Adsorbed water $\underline{a} = 5,9$ mm/g	$-40$ — $100$	"	11,4	$10^{18}$
same	below $-100$	"	8,2	$10^{15}$
Adsorbed water $\underline{a} = 20$ mm/g	$-40$ — $100$	"	14,6	$10^{22}$
same	below $-100$	"	4,3	$10^9$
Adsorbed water $\underline{a} = 50$ mm/g	$-40$ — $100$	"	16,7	$10^{24}$
same	below $-100$	"	2,9	$10^8$
Adsorbed water	0— $40$	Conductivity	23,5	—

for adsorbed water. A preliminary analytical calculation convinced us that the shift in the relaxation maximum due to the heterogeneity of our system lies within the limits of errors of measurement.

From the theory of absolute reaction rates [11] it is known that the relation of  $\log f_{\max}$  to  $1/T$  should be represented by a straight line, the slope of which is the activation energy of the process. As we observed not only the Debye relaxation maximum  $\epsilon''$ , but also the Wagner maximum due to electroconductivity in the adsorbed layer, we were able to determine activation energies for the polarization process and for the process of electroconductivity in the adsorbed layer. Figure 2 gives the relation of  $\log f_{\max}$  to  $1000/T$  for water adsorbed on K-2 silica gel for the polarization process (Curves 1, 2, and 3) and for the electroconductivity process (Curve 6). Also, we give analogous relations, based on data from the literature, for ordinary water and ice [12] (Curves 4 and 5). Activation energies and frequency factors determined from Fig. 2 are given in the table.

An examination of Fig. 2 and the table shows that there is a sharp change in the activation energy of adsorbed water at  $-100^\circ$ , which appears to indicate structural changes occurring at this temperature. In its activation energies, both for electroconductivity and for polarization, adsorbed water approaches ice. It may here be mentioned that according to Bot and Montagner [5], whose measurements were made at room temperature, the activation energy for the polarization process is 12.5 kcal/mole, which, when compared with our results indicates absence of any sharp change in the properties of adsorbed water as we pass through the ordinary melting point. Some increase in activation energy, observed as adsorption increases, apparently indicates a high degree of localization of dipoles adsorbed in the first layers when new upper layers are formed. This behavior may be a second cause for the reduction noted above in the rate of growth of  $\epsilon_0$  as  $\alpha$  increases. It is interesting to note that in the paper [4] the temperature  $-100^\circ$  is interpreted as the melting point of adsorbed water in the dissociated state.

#### SUMMARY

1. The Debye dispersion of the dielectric permeability DP of adsorbed water on finely and coarsely porous silica gels was investigated by the method of frequency variation over wide ranges of adsorption, temperature, and frequency.

2. It was shown that, in the study of dielectric isotherms of adsorption, it is essential to use static DP values, which can be obtained from dispersion measurements.

3. From experimental measurements of frequencies of relaxation maxima in the regions of Wagner and Debye dispersion, activation energies of adsorbed water were found for the processes of electroconductivity and polarization.

4. It was shown that the activation energy for the polarization process in adsorbed water undergoes no sudden change at  $0^\circ$ , but changes at  $-100^\circ$ .

5. The activation energy of adsorbed water is close to the values obtained for ordinary ice.

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# ELECTRON CHARGES OF BONDS IN ETHYLENE, ALLENE AND BENZENE

G. V. Bykov

The author [1] proposed the following equation for the relation between electron charges  $A$  of C-C and C-H bonds of the hydrocarbons  $C_nH_m$  and the heats of breakdown to the elements  $H_{C_nH_m}^{el}$

$$8,054 \sum A_{CC}^{\sigma} + 32,308 \sum A_{CH}^{\sigma} - 1,54 \sum A_{CC}^{\pi} - 9,38 \sum A_{CH}^{\pi} = H_{C_nH_m}^{el} + 52,089m + 32,216n. \quad (1)$$

The superscripts to  $A$  indicate the character of the charge ( $\sigma$  or  $\pi$ ), and the subscripts indicate the type of bond.

For the calculation of  $\sum A$ , apart from Equation 1, three other independent equations containing summations of electron charges of bonds are necessary; two equations are obvious:

$$\sum A_{CC}^{\sigma} + \sum A_{CH}^{\sigma} = N^{\sigma}; \quad (2)$$

$$\sum A_{CC}^{\pi} + \sum A_{CH}^{\pi} = N^{\pi}, \quad (3)$$

in which  $N^{\sigma}$  and  $N^{\pi}$  are, respectively, the numbers of  $\sigma$ - and  $\pi$ -electrons in the given molecules.

The following equation can also be applied in the calculation:

$$\nu_{CH}^{1,4} = 3,553 \cdot 10^4 \cdot A_{CH}^{\sigma\pi}, \quad (4)$$

in which  $\nu$  is the frequency of the symmetrical vibration of the C-H bond [1] and  $A_{CH}^{\sigma\pi}$  is the total electron charge of the C-H bond:

$$A_{CH}^{\sigma\pi} = A_{CH}^{\sigma} + A_{CH}^{\pi}. \quad (5)$$

Experimental values required in the calculation and the numbers  $N^{\sigma}$  and  $N^{\pi}$  are given in Table 1. From the total electronic charges of bonds it is easy to pass to charges of individual bonds (Table 2).

For verification let us use the equation:

$$l_{CC} = 1,542 - 0,149 \cdot A_{CC}^{\pi}, \quad (6)$$

TABLE 1

Numerical Values of Characteristics of Ethylene, Allene, and Benzene Molecules

Compound	$H_{C_n} H_m$ (kcal/mole) [2]	$N^\sigma$	$N^\pi$	$\nu_{CH}$ ( $cm^{-1}$ ) [3]	$l_{CC}$ (A) (exptl)	$l_{CC}$ (A) (calc.)
Ethylene	-12.496	10	2	3019	1.330 [4]	1.339
Allene	-45.92	12	4	2992	1.309 [5]	1.318
Benzene	-19.820	24	6	3063	1.397 [6]	1.400

which permits us to calculate the C-C bond length [7]. Substituting  $A_{CC}^\pi$  in Equation 6 from Table 2 we find  $l_{CC}$  (calc'd.). From the last two columns of Table 1 we see that the departure of the results of our calculation from experimental spectroscopic values is less than 0.01 Å, i.e., less by a factor of 2-3 than the inaccuracies inherent in electronographic and x-ray methods. We may note also that Scherr [8] found that  $A_{CC}^\pi = 1.333$   $\pi$ -electrons for ethylene, which is close to our value.

TABLE 2

Electron Charges of Bonds (in electrons)

Compound	$A_{CC}^\sigma$	$A_{CC}^\pi$	$A_{CC}^{\sigma\pi}$	$A_{CH}^\sigma$	$A_{CH}^\pi$	$A_{CH}^{\sigma\pi}$
Ethylene	2.256	1.364	3.620	1.936	0.159	2.095
Allene	2.363	1.500	3.863	1.819	0.250	2.069
Benzene	1.910	0.952	2.862	2.090	0.048	2.138

## SUMMARY

1. The  $\sigma$ - and  $\pi$ -electron charges of bonds in ethylene, allene and benzene were calculated.
2. With the aid of the calculated values of the  $\pi$ -electron charges of C-C bonds, C-C bond lengths were calculated for these three compounds. The results of the calculation are in satisfactory agreement with experimental data.

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\*Original Russian pagination. See C. B. Translation.

# POLYMERIZATION OF ACRYLONITRILE IN PRESENCE OF TRIBUTYLBORINE

G. S. Kolesnikov and L. S. Fedorova

The work of Ziegler on the polymerization of ethylene in presence of triethylaluminum is now well known, and as a result of this work a method of polymerizing ethylene without the use of pressure has been developed [1]. Before Ziegler's work it was considered that ethylene is among the unsaturated compounds which polymerize with difficulty, and it seemed that the catalysts that could be used for polymerizing ethylene in absence of pressure might be applicable to the polymerization of other polymerizable compounds, e.g., acrylonitrile. It was found, however, that in presence of triethylaluminum promoted by titanium tetrachloride, acrylonitrile does not polymerize, and our attempts to prepare polyacrylonitrile in this way were unsuccessful. The absence of catalytic activity in triethylaluminum for the polymerization of acrylonitrile may be explained by the formation of a complex between triethylaluminum and acrylonitrile with the aid of a pair of electrons held in common by the nitrogen and aluminum atoms. It would appear that such a complex is so stable that it cannot catalyze the polymerization process, even in presence of a promoter.

On the assumption that catalytic activity similar to that of aluminum compounds should be possessed by compounds of elements having an outer electron shell of the same configuration as that of aluminum, i.e.,  $s^2, p^1$ , we examined the use of a boron compound, namely tributylborine, as a catalyst for the polymerization of acrylonitrile. It is known that boron trifluoride can be used as a catalyst in the alkylation of aromatic compounds with alcohols. It may be supposed that in boron compounds the tendency for complex-formation with oxygen-containing (and apparently also nitrogen-containing) substances is not great and the deactivation of boron-containing catalysts will not occur or will occur to a smaller extent.

Preliminary experiments showed that, in absence of promoter, the polymerization of acrylonitrile in presence of tributylborine proceeded in low yield (5-6%) and that the use of titanium tetrachloride as promoter did not affect the catalytic activity of tributylborine. An effective promoter of the polymerization of acrylonitrile in presence of tributylborine was found in the ether complex of boron trifluoride, which by itself does

TABLE 1

Polymerization of Acrylonitrile in presence of Tributylborine  
(Concentration of acrylonitrile in xylene 13.3 g/100 ml; reaction temperature 70°; duration of reaction two hours)

Concentration of tributylborine (moles % on acrylonitrile)	Concentration of boron trifluoride etherate (moles % on acrylonitrile)	Yield of polymer (%)	Specific viscosity of 0.5% solution of polymer in dimethylformamide
1.0	2.0	35.0	0.181
2.0	1.0	40.4	0.105
2.0	2.0	66.5	0.109
2.0	4.0	44.0	0.167
2.0	8.0	44.2	0.136

not bring about the polymerization of acrylonitrile under our conditions. In the present investigation we attempted to determine the effects of various factors on the course of the polymerization of acrylonitrile in presence of tributylborane and boron trifluoride etherate, the main attention being turned to the effects of concentration of catalyst and promotor on the yield and molecular weight of the polyacrylonitrile obtained.

TABLE 2

Polymerization of Acrylonitrile in presence of Tributylborane

Duration of reaction (hours)	Yield of polymer (%)	Specific viscosity of 0.5% solution of polymer in dimethylformamide
2	35.0	0.181
4	37.7	0.264
6	82.0	0.377

Experimental conditions and results are given in Tables 1 and 2.

It will be seen from Table 1 that the best yield of polyacrylonitrile was obtained for equimolecular proportions of catalyst and promotor and for a concentration of catalyst of 2%. Increase in concentration of promotor to above 2% resulted in some reduction in the yield of polyacrylonitrile, but the molecular weight of the polymer was increased. One of the causes of low yield of polymer could be insufficient time for the polymerization reaction. To check this possibility we carried out experiments in which catalyst and promotor concentrations were constant and equal to 1 and 2 mole % respectively, the temperature was 70°, and 13.3 g of acrylonitrile was present in 100 ml of xylene. The results

of these experiments are given in Table 2.

It can be seen from Table 2 that increase in the duration of polymerization results in increase in the yield of polyacrylonitrile and increase in its molecular weight. Other conditions being equal, lowering of reaction temperature to 50° results in lower yields of polyacrylonitrile, but has little effect on the molecular weight of the polymer. At a concentration of catalyst of 1 mole % and a concentration of activator of 2 mole %, the yield of polyacrylonitrile was 27.7% after two hours, and the specific viscosity of a 0.5% solution of the polymer in dimethylformamide was 0.131 (all viscosities were determined at 20°); at 70° these values were 35.0% and 0.181, respectively.

#### SUMMARY

It was found that acrylonitrile polymerizes in presence of tributylborane activated by the boron trifluoride ether complex.

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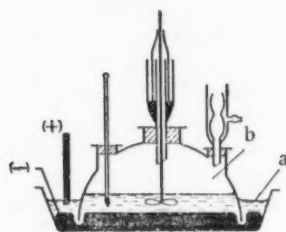
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## HYDRODIMERIZATION OF ACRYLONITRILE

I. L. Knunyants and N. S. Vyazankin

Whereas the reductive dimerization of cinnamic [1], pentadienoic [2], sorbic [3], and some other acids has been investigated in fair detail, the possibility of the hydrodimerization of the simplest  $\alpha,\beta$ -unsaturated acids has remained obscure. Attempts to obtain hydrodimers by electroreduction of acrylonitrile [4] and acrylic and methacrylic esters [5, 6] at cathodes of the mercury type have led to the formation of polymeric substances. There are also isolated communications about the formation of adiponitrile in yields of up to 5% in the reduction of acrylonitrile with magnesium amalgam in methanol [7] and with sodium amalgam in water [8]. In 1954 Knunyants, Gambaryan, and Vyazankin showed [9] that the reductive dimerization of acrylonitrile could be effected in high yield by indirect electrochemical reduction in acid media. The present work forms a further development of investigations in this field.



The apparatus for studying reductive dimerization consists of a combination of an electrolyzer A for preparing amalgam and a reaction vessel B, in which the amalgam is decomposed (see figure). The vessel B (bottomless) is immersed in mercury to a depth of 5-7 mm. The mercury was made the cathode (surface area 1.80 dm<sup>2</sup>), and it acted as a seal, preventing mixing of electrolyte and reaction mixture. The surface of the amalgam in the reaction vessel was 2.35 dm<sup>2</sup>. The dependence of the yield of adiponitrile on the acidity of the medium was studied by reducing 0.2 mole of acrylonitrile with potassium amalgam in 100 g of hydrochloric acid of various concentrations (Table 1). In order to maintain the initial concentration, the calculated amount of 35.38% hydrochloric acid was added continuously to the mixture. Electrolysis of 40% potassium hydroxide solution was carried out with a cur-

rent of 7 amp for three hours at 14-16°.

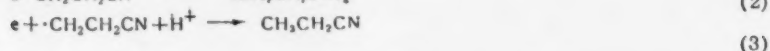
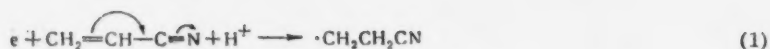
TABLE 1

Initial HCl concentration (%)	3	6	10	15	20	25*
Rate of addition of 35.38% HCl (ml/minute)	0.28	0.32	0.36	0.40	0.44	0.48
Yield of adiponitrile (%)	35.9	48.9	51.2	46.3	47.8	31.4

\* There was much salt deposition, which contaminated the amalgam surface.

It was found that the phenomenon of hydrodimerization is dependent on the nature of the amalgam and acid (see Experimental). Reductive dimerization apparently proceeds by addition of an electron and a hydrogen ion to an adsorbed molecule, and it can be represented by the scheme:





As hydrodimerization is not accompanied by polymerization and, as is well known, acrylonitrile is a highly sensitive reagent toward free radicals [10], it must be supposed that the radicals formed in Reaction 1 are adsorbed on the surface and do not pass into solution. In accordance with this scheme it is found that factors reducing the surface concentration of radicals lead to preferential occurrence of Reaction 3. Thus, at low concentrations of acrylonitrile in the reaction mixture (Table 2) and at low currents (Table 3) the yield of adiponitrile falls appreciably.

Investigation showed further that addition of alcohols or dioxane to the reaction mixture greatly reduces the yield of adiponitrile. This fact can be explained both by change in the structure of double electric layer, in conditions of adsorption of acrylonitrile, etc., and also by purely chemical interaction of adsorbed radicals with the added substances. It is known that free radicals of the type  $\cdot\text{CH}_2\text{CH}_2\text{COOCH}_3$  react with alcohols with formation of propionic acid derivatives [11]. However, the last supposition must be rejected, for in the reductive dimerization of acrylonitrile in presence of ethanol deuterated in the  $\text{CH}_2$  group the propionitrile formed was undeuterated. The absence of polymerization and the experiment with deuterium-containing alcohol show that the properties of radicals adsorbed on an amalgam differ considerably from the properties of free radicals in solution. The reductive dimerization of carbonyl compounds at mercury and lead cathodes is sometimes accompanied by the formation of organometallic compounds [12]. The absence of this phenomenon in our case may be explained by the instability of the organomercury compounds under the conditions of indirect electroreduction. In order to verify this suggestion 3,3'-mercuridipropionitrile (m.p. 50-51°, from acetic acid) was prepared by reaction between 3-iodopropionitrile and 0.5% sodium amalgam. The compound was not affected by treatment with potassium amalgam in aqueous acetic acid.

TABLE 2\*

Composition of reaction mixture			Acrylonitrile content (%)	Yield of adi- ponitrile (%)	Unchanged acrylonitrile (%)
20% HCl (g)	Acrylonitrile				
	(g)	(mole)			
183	5.3	0.1	2.8	18.1	0.7
183	10.6	0.2	5.5	30.2	2.3
183	15.9	0.3	8.0	48.5	5.0
183	18.6	0.35	8.8	55.3	5.3
183	21.2	0.4	10.4	62.2	6.5
183	26.5	0.5	12.7	53.6	12.9

\* Electrolysis of 40% of KOH solution was carried out at 9 amp and 14-16° to an alkaline reaction of the reaction mixture to phenolphthalein.

TABLE 3\*

Current (amp)	2,5	4	6	8	9	11
Duration of process (hours)	11	7	5	3 <sup>3</sup> / <sub>4</sub>	3	2 <sup>1</sup> / <sub>2</sub>
Yield of adiponitrile (%)	15.4	28.7	31.7	41.3	61.0	53.1

\* A mixture of 0.4 mole of acrylonitrile and 183 g of 20% HCl was reduced. The electrolyte was 40% KOH at 14-16°. The end of reaction was determined with phenolphthalein.

## EXPERIMENTAL

Hyrodimerization of Acrylonitrile. A mixture of 0.4 mole of acrylonitrile and 1 mole of 20% HCl solution was prepared in the vessel B. The mixture was treated with potassium amalgam prepared by electrolysis of 40% KOH solution at 9 amp and 14-16° until there was an alkaline reaction to phenolphthalein (three hours). The mixture was then acidified and steam-distilled. The distillate was saturated with potassium carbonate, and the organic layer was separated and dried. The products from five parallel experiments were combined and fractionated through a column. As calculated for a single experiment, we obtained 1.3 g of acrylonitrile, b.p. 74-77° and  $n_D^{20}$  1.3892; 0.7 g of a fraction of b.p. 77-95° and  $n_D^{20}$  1.3742 and 4.8 g of propionitrile, b.p. 95-98° and  $n_D^{20}$  1.3673.

The residue from the steam distillation was extracted with chloroform, and 13.2 g (62.2%) of adiponitrile was isolated: b.p. 138-140° (3 mm);  $n_D^{20}$  1.4410;  $d_4^{20}$  0.9514.

Found %: C 66.42, 66.47; H 7.39, 7.33; N 25.94.  $C_6H_8N_2$ . Calculated %: C 66.65; H 7.45; N 25.89

No amines or polymeric substances were found in the reaction products. Under the same conditions with sodium amalgam, the yield of adiponitrile was 37.4%. When the hydrochloric acid was replaced by the equivalent amounts of 30% acetic acid, 23% formic acid, 25% sulfuric acid, and 40% phosphoric acid, the yield of adiponitrile was reduced to 30.0%, 36.3%, 39.3%, and 49.7%, respectively.

Hyrodimerization of Acrylonitrile in Presence of Deuterated Ethanol. The conditions were as in the preceding experiment, but 12.4 g of deuterated ethanol [12] containing 8450  $\gamma$  of deuterium in the  $CH_2$  group was added. When reaction was complete, 3.4 g (15.7%) of adiponitrile was isolated in the usual way. To 96 ml of distillate obtained in the steam distillation, 25 ml of alcohol was added, and the fraction boiling below 71° was removed through a column. Potassium hydroxide (17 g) was added to the residue, which was boiled for eight hours and then evaporated to dryness. The residue was dissolved in 60 ml of water and again evaporated. This operation was repeated five times, after which acidification with dilute hydrochloric acid and extraction with ether gave 10.7 g of a product, fractionation of which gave 5.4 g of propionic acid, b.p. 139-141°; anilide m.p. 105° (from alcohol). The water obtained by combustion of the acid had no excess of density.

## SUMMARY

1. A method was developed for the reductive dimerization of acrylonitrile to adiponitrile.
2. The reductive dimerization of acrylonitrile occurs at the surface of the amalgam. The intermediately formed radicals are not desorbed into the body of the solution and do not possess the properties characteristic of free radicals in solution.
3. Reductive dimerization does not proceed through the stage of formation of organomercury compounds.

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\*Original Russian pagination. See C. B. Translation.

## CURRENT EVENTS

### INTERNATIONAL CONGRESS ON CATALYSIS IN PHILADELPHIA

N. I. Shuikin

An International Congress on Catalysis was held in Philadelphia September 10-14, 1956. It was organized by the Philadelphia Catalysis Club, supported by the Chicago Catalysis Club, Pennsylvania University, and the National Science Foundation. Its sponsors included also the international Union of Pure and Applied Chemistry, and considerable financial support in this important undertaking was given by thirty-five American chemical, oil, and metallurgical firms, including twenty very large oil companies.

Seven hundred delegates from twenty-two countries took part in the Congress; they included scientists, technologists— including oil technologists— and representatives of business concerns. The largest groups of delegates were from the US, Britain, Canada, the Federal German Republic, and France. The honorary presidents of the Congress were Prof. Sir. Eric Rideal, Professor Sir Hugh Taylor, and Dr. E. J. Houdry.

The Soviet scientific delegation had four members: N. I. Shuikin, Corr. Member of Acad. Sci. USSR (leader of delegation), Prof. K. V. Topchieva (Moscow State University), Prof. F. F. Volkenshtein, and M. F. Nagiev, Fellow of Academy of Sciences of Azer. SSR. Our delegation arrived in New York by air on September 8 and traveled to Philadelphia by train on the same day. On the next morning we met leading members of the Organizing Committee of the Congress— Drs. A. Farcas, H. Heinemann and A. W. Grosse. Our relations were very friendly and unconstrained.

We presented the following four papers at the Congress: 1) N. I. Shuikin (N. D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the USSR), "Catalytic Transformations of Cyclic Hydrocarbons over Group VIII Metals" (in English); 2) K. V. Topchieva (Department of Physical Chemistry, Moscow State University), "Part Played by Surface Compounds in Catalytic Dehydration of Alcohols over Alumina and Silica-Alumina Catalysts" (in English); 3) F. F. Volkenshtein (Institute of Physical Chemistry of the Academy of Sciences of the USSR), "Mechanism of the Catalytic Action of Semiconductors" (in French); 4) M. F. Nagiev (Petroleum Institute of the Academy of Sciences of Azer. SSR), "Determination of Material Balance of Complex and Multistage Processes with Recycling" (in English).

Apart from these papers, the Soviet delegation submitted the following six papers to the Organizing Committee for publication in the Transactions of the Congress: 1) A. A. Balandin "Nature of Active Centers and Kinetics of Catalytic Dehydrogenation"; 2) N. I. Kobozev "Physical and Mathematical Principles underlying the Theory of Active Centers. The Atom and the Crystal in Catalysis"; 3) N. I. Kobozev "Catalytic and Magnetic Properties of Highly Rarefied Layers. The Electron in Catalysis"; 4) N. I. Kobozev "Catalyst and Enzyme. The Aggravation Effect in Catalysis"; 5) V. P. Lebedev "Thermal Activation of Platinum Catalysts"; 6) O. M. Poltorak "Catalytically Active Ensembles of Metallic Ionic Crystals."

The work of the Congress was carried out in morning and evening sessions in a well-appointed auditorium which seated 750. Detailed abstracts of all papers had been published beforehand and distributed to the participants.

The Congress was opened on the morning of September 10 by a welcoming speech from the mayor of Philadelphia and representatives of the organizing bodies. Sir Hugh Taylor (Princeton University) then gave the Opening Address, and was followed by Sir Eric Rideal (Imperial College of Science and Technology, England), who spoke on "Heterogeneous Catalysis: Milestones along the Way" and further by Prof. R. L. Burwell (Northwestern University, Evanston, Ill.) whose subject was "Stereochemistry and Heterogeneous Catalysis." At this Opening Session the chairman was Dr. A. Farcas, director of the program of the Congress.

The working program of the Congress was divided into four symposia, which took place in succession without any division into simultaneous sections. Each symposium included special sections.

Symposium I: "Chemistry and Physics of Solid Catalysts," divided into 1) Hydrogenation and Hydrogen-exchange Reactions (8 papers); 2) Physical Properties of Catalysts (7 papers); 3) Electronic Properties and Catalytic Activity (9 papers).

Symposium II: "Homogeneous Catalysis and Related Effects," divided into 1) Acid-Base Catalysis (3 papers); 2) Catalysis by Metal Compounds (3 papers); 3) Reaction Kinetics (3 papers); 4) General (3 papers).

Symposium III: "Surface Chemistry and its Relation to Catalysis," divided into 1) Corrosion and Surface Reactions (4 papers); 2) Chemisorption of Oxygen (4 papers); 3) Adsorption Phenomena (4 papers).

Symposium IV: "Techniques and Technology of Catalysis." This was the biggest symposium; twenty-eight papers were given in the sections: 1) Catalytic Cracking and Cracking Catalysts (6 papers); 2) Isomerization and Other Reactions of Hydrocarbons (3 papers); 3) Reactions of Carbon Monoxide (4 papers); 4) Tracer and Other Techniques (5 papers); 5) Miscellaneous Catalytic Reactions (10 papers).

The Organizing Committee decided that, as the papers of the Soviet delegation were not covered by the program, a second evening session should be held on September 11 for the presentation and discussion of these. In spite of the late hour, the auditorium was overcrowded. The presentation of the papers went satisfactorily, and the papers prompted various questions and a lively discussion, with friendly approval of the audience. Together with the other papers they will be published in the Transactions of the Congress, which will appear as Volume 9 of "Advances in Catalysis."

As it is impossible for us to discuss all of the eighty papers read at the Congress, we shall refer only to those which in some degree characterize original lines of work on catalysis in foreign countries.

1. American chemists are devoting much attention to stereochemical investigations in the field of catalysis. Thus, in R. L. Burwell's paper "Stereochemistry and Heterogeneous Catalysis" an attempt is made to present those aspects of the stereochemistry of heterogeneous catalysis which might be able to throw light on the mechanism of heterogeneous catalytic reactions. It has long been known that the catalytic hydrogenation at room temperature of acetylenic hydrocarbons into olefins, of olefins into paraffins, and of aromatic hydrocarbons into cyclohexanes includes an initial stage of *cis* addition. However, recent work by this author has shown that the predominating *cis* addition is usually accompanied by some *trans* addition. At high temperatures *trans* addition may be predominant. It was shown, for example, that the reaction of isotopic exchange between deuterium and (+)-3-methylhexane over nickel and palladium catalysts at above 100° results in the racemization of the optically active hydrocarbon. Similar results on the conditions of the formation of *cis* and *trans* forms of hydrocarbons in catalysis were reported by S. Siegel and M. Dunkel (Arkansas University) in the paper "Stereochemistry of the Hydrogenation of the Isomers of Dimethylcyclohexene and Xylene."

2. Papers on the electronic theory of catalysis occupied an important place at the Congress. In his introductory remarks, Sir Hugh Taylor had already discussed the promising nature of this direction in catalysis. Here we must first of all refer to the paper of W. E. Garner (Bristol University) "Electron-transfer Processes and Catalysis." This paper mainly concerned the part played by structural defects of the lattice in adsorption and catalysis. The author confined himself to a consideration of the ionic bond in chemisorption, ignoring the possibility of homopolar bonds of various types which, as F. Volkenshtein has shown, also occur in chemisorption. A paper of undoubted interest was that of G. M. Schwab (Technical University, Munich) "Photochemical and Kinetic Studies of Electronic Reaction Mechanisms," in which he discussed the effect of irradiation on the catalytic activity of a semiconductor—in this case germanium. In his paper "Endothermic Chemisorption and Catalysis," J. H. de Boer (Holland) proved the possibility of endothermic adsorption. Such adsorption is observed in the exchange of hydrogen for deuterium over alumina, in the transformations of para-hydrogen over sodium chloride, and in isomerization reactions over metals poisoned with sulfur. If de Boer's views are confirmed in other cases, his work will have great fundamental significance.

3. At the session devoted to cracking catalysts, great interest was shown in the paper by W. T. Barrett, M. G. Sanchez and J. G. Smith (Baltimore) "Phase Transformations in Silica-Alumina Catalysts." The authors studied phase transitions in synthetic silica-alumina catalysts containing 25% of alumina when treated thermally (750-1250°). It was shown that, under these conditions, synthetic silica-alumina gives a crystallized  $\gamma$ - $\text{Al}_2\text{O}_3$ .



structure and mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). The phase transition is accompanied by loss of catalytic activity and breakdown of the porous structure of the catalyst.

4. There was much interest in papers on tracer studies of the mechanism of the catalytic isomerization of hydrocarbons. Here we must mention the paper of H. Pines and A. E. Shaw (Ipatiev High-pressure Laboratory, Northwestern University, Evanston, Ill.) entitled "Hydroisomerization of ethylcyclohexane- $\alpha$ - $\text{C}^{14}$ ". The authors made a systematic study of the mechanism of the hydroisomerization of ethylcyclohexane labeled in the  $\alpha$ -position of the side chain with  $\text{C}^{14}$  over a nickel-silica-alumina catalyst at  $360^\circ$  and 25 atm of hydrogen in a flow system. Investigation of the alkylcyclohexane composition of the catalyzate and the distribution of radioactivity between ring and side chain showed that a carbonium ion mechanism operated with repeated contraction and enlargement of the ring.

We must mention also the very interesting paper by V. I. Komarevsky and D. Miller (Illinois Institute of Technology, Chicago) entitled "Hydrogenation with Metal Oxide Catalysts." The authors showed that vanadium and chromium oxides, which are extensively used as dehydrocyclizing and dehydrogenating catalysts, can catalyze also hydrogenation reactions. It was shown that, in presence of either of these oxides, acetylenic hydrocarbons, dienes, and olefins are hydrogenated at ordinary pressure. This reaction is accompanied by partial isomerization of the chain. The optimum temperature is  $400^\circ$ ; the yield of hydrogenation products attains 77-98%. Aromatic hydrocarbons are hydrogenated only in presence of vanadium oxide at  $475^\circ$  and 115 atm.

A paper by one of the honorary presidents of the Congress, Dr. E. J. Houdry, author of the well-known process of cracking petroleum distillates in presence of silica-alumina catalysts, was of exceptional interest; it was entitled "Practical Catalysis and its Effect on our Generation." The author gave a very instructive historical review of the development of the most important investigations in catalysis, particularly catalytic cracking. He devoted much attention to the new line of work which he developed in 1948: the problem of complete (smokeless) combustion of fuel in presence of catalysts and the question of the complete combustion of fuel in internal-combustion engines in connection with the general contamination of the atmosphere and increase in the incidence of cancer.

In his paper E. J. Houdry referred to the work of Dr. Paul Cotine, in which it is shown that, under the influence of the sun's rays, even such harmless hydrocarbons as alkanes become active and cause the appearance of cancerous growths in the lungs of animals. Houdry showed that the hydrocarbons and carbon monoxide in automobile exhaust gases can be oxidized with the aid of catalysts before they pass into the atmosphere, and can in this way be made harmless. This result can be achieved with the aid of an arrangement similar to a gas turbine which contains the catalyst "Oxycat" and can be attached to any automobile. The speaker stated that the catalyst chamber attached to the gas turbine working on exhaust gas ensured the production of thermal energy at a constant level for 16,000 hours (more than 666 days). This example shows that catalysis can free us from the limitations imposed on us by flame combustion. The final solution of this problem will have a colossal economic effect, make the atmospheres of industrial centers much healthier, and, in Houdry's opinion, lead to a considerable reduction in the incidence of cancer.

A very interesting paper was given by A. G. Oblad and H. Shalit (Houdry Process Corp., Marcus Hook, Pa.) on "Technology of Catalysis in the Petroleum Industry." The authors discussed the chemical, technical and economic characteristics of the present catalytic processes used in the petroleum-refining industry of the US and other countries. Numerical data were presented on the evolution and present state of this enormous vital industry.

The work of the Congress was completed by a session on organization, in which the organizers of the Congress and the leaders of foreign delegations took part. At this session it was agreed that 1) the First International Congress on Catalysis had been successful and had dealt satisfactorily with the tasks which it had set itself; 2) it is desirable to have further congresses at three-yearly intervals; 3) the next International Congress on Catalysis will be held in Europe, probably in Paris, in 1959. In our opinion, the Third International Congress on Catalysis in 1962 should be held in Moscow.

#### Visit to Pennsylvania and Columbia Universities

With the help of Dr. Houdry and Prof. K. A. Krieger, the Soviet delegation was able to visit the chemical departments of Pennsylvania and Columbia universities.



The University of Pennsylvania is one of six universities in Philadelphia. It is a private teaching institution, built and maintained with funds provided by business circles and donations from certain former students of the university. The normal chemistry course occupies five years. Work is centered on the laboratory, in which much attention is devoted to micro and semimicro methods. The students are given good training also in glass-blowing and the construction of laboratory apparatus, for which purpose training in lathe work and other such techniques is given. The training of senior scientific workers and high-school teachers is carried out in the so-called Graduate School of Arts and Sciences, which is similar to our "aspirantur." The time required for qualification is 3-5 years and, depending on the course selected and the success of the student, it is completed with the conferment of the degree of Master of Arts (A.M.), Master of Science (M.S.), or Doctor of Philosophy (Ph. D.).

The teaching staff carry out research work, both on their own and in collaboration with graduates and graduate students (our "aspirants"). We learned something of work being carried out on the mechanism of cracking *n*-butane in presence of radioactive iodine, on exchange of hydrogen for deuterium and tritium in alkanes (butane and pentane), and on exchange of deuterium for tritium.

The professors and lecturers were extremely obliging and helpful. They expressed a desire to exchange reprints of papers, and they provided us with the plans of their training schemes for senior scientific personnel. We parted friends.

#### Columbia University (New York)

With the kind assistance of Dr. E. J. Houdry and senior staff of the Houdry Process Corporation, Drs. A. G. Oblad, C. L. Thomas, and S. S. Peevy, we were able to acquaint ourselves with the teaching and research laboratories of the chemistry department of Columbia University. At the present time the "chairman" of this department is Prof. C. L. Thomas, who specializes in colloid chemistry.

Here, as in other American universities, teaching work begins on September 24. There were, therefore, no students in the laboratories and only a few teachers and laboratory staff were working.

We were first shown a well-stocked departmental library and a departmental museum on the history of chemistry containing portraits of prominent chemists and physicists with short descriptions of their more important investigations. Russian chemists were represented by N. N. Zinin and D. I. Mendeleev. The large chemical lecture theater with wide rotating slates and an enormous screen for the epidiascope and the projection of scientific films created a very favorable impression.

Undergraduate studies of characteristic chemical reactions by semimicro methods were made not only in the analytical laboratories but also in the general and inorganic laboratories. In the research laboratories work was being carried out with deuterium, tritium, radio-iodine, and  $C^{14}$ . Interesting investigations were being carried out on the peculiarities of the triple bond in crystalline acetylene (m.p.  $-81^\circ$ ) with the aid of the infrared spectrometer, and a spectroscopic investigation was being carried out on liquid sulfur with the object of establishing the temperature-dependence of the length of the chain of sulfur atoms. The polymerization of alkenes (propene, butenes, pentenes) at pressures of up to 13,000 atm was being studied. The scientific laboratories were well provided with modern apparatus. There were special places and special apparatus for work with radioactive substances. A notable feature was the use of chemical vessels made of polyethylene and polychlorotrifluoroethylene ("organic platinum"). In Columbia University, we were again most courteously and cordially received by our American fellow-scientists.

Returning to Philadelphia, with the aid of influential American members of the Organizing Committee of the Congress we were able to visit an oil-refining works of the Atlantic Refining Co. with its large plant for catalytic cracking and catalytic reforming (platforming). This work treats 150,000 barrels (1 barrel = 40 gallons = 151.4 liters) per day; it produces motor fuel of octane numbers 80 and 90-92. We visited also the research laboratories of the Houdry Process Corporation—a large research institute occupied with the selection and development of catalysts of various types for the chemical and oil-refining industries. The institute provides industry with catalysts through its catalyst works at Polesboro.

The participation of the Soviet delegation in the work of the Congress and its visits to the two American universities and to works and industrial research institutes enabled it to make scientific contacts with several outstanding American scientists and technologists, and also with eminent scientists from Great Britain, France, the German Federal Republic, Japan and other countries. The organizers of the Congress acknowledged that Soviet scientists made a very significant contribution to the results of the Congress.

## CONFERENCE ON THE STANDARDIZATION OF LABORATORY GLASSWARE

In the N. D. Zelinsky Institute of Organic Chemistry, toward the end of 1956, a conference was held on the standardization of laboratory glassware fitted with ground joints for use in work on organic chemistry. The Conference was called by the Division of Chemical Sciences of the Academy of Sciences of the USSR. Representatives of seventeen different organizations took part: Academy organizations, namely, the Division of Chemical Sciences, the Kazan Affiliated Institute, the N. D. Zelinsky Institute of Organic Chemistry, the Institute of Heteroorganic Compounds, the N. S. Kurnakov Institute of General and Inorganic Chemistry, the Geochemical Institute, the Petroleum Institute, and the Institute of Physical Chemistry; other educational and research establishments, namely, the Chemical Department of the M. V. Lomonosov Moscow State University, the M. I. Kalinin Moscow Institute of Nonferrous Metals and Gold, the S. G. Ordzhonikidze Chemical and Pharmaceutical Research Institute, the Institute of Biological and Medicinal Chemistry of the Academy of Medical Sciences of the USSR, and the Research Institute of the Meat Industry; and also the Klin laboratory-apparatus factory "Laborpribor." The participants of the Conference inspected the permanent exhibition of laboratory glassware with standard joints developed by the Joint Committee of the Institutes of Organic Chemistry and of Heteroorganic Compounds.

In his introductory address, the chairman of the Conference, M. I. Kabachnik, Corr. Mem. Acad. Sci. USSR, of the Institute of Heteroorganic Compounds remarked that our times were characterized by the extensive adoption of new techniques in all fields of Soviet scientific and industrial activity, this move being made not merely so as to be "in the fashion," but out of sheer necessity in order to effect a cardinal improvement in the productivity of labor. In the resolutions of the Twentieth Congress of the Communist Party of the Soviet Union a great deal of attention had been devoted to the introduction of new techniques in industry, agriculture, and scientific investigation. Scientific institutes that were to take up leading places in the development of new ideas could not tolerate backwardness in technical methods, and yet chemists were still using laboratory ware of old design belonging to the first half of the century. It had now become absolutely essential to raise the level of the technical equipment of our laboratories by the provision of modern glassware, standardized to a greater extent than had been done up to now. The establishment of the manufacture of standard joints in the USSR has greatly facilitated the solution of this problem.

The report prepared by the Committee on the Standardization of Laboratory Ware with Standard Joints was read by the chairman of the Committee, O. D. Sterligov (Institute of Organic Chemistry). He pointed out that the use of standard joints in laboratory practice has many advantages over corks, rubber stoppers, and nonstandard joints: the scope of the worker is widened and he can assemble many pieces of apparatus from a small number of parts.

The use of standard joints increases the possibilities of standardization and leads, on the one hand, to an increase in the productivity of glassblowers, and improvement in the quality of the product, and on the other hand, to a widening of the scope of the experimenter, increasing his productivity and raising the cultural value of his labor.

The speaker then stated that the advantages of standard joints had been realized abroad 25-30 years ago, when the manufacture of such joints was begun. However, the possibilities of standard joints had been exploited far from completely, even by the firm of Schott, with its worldwide reputation, for this firm still offered various articles of obsolete design. In 1949-50 the Klin factory began to produce apparatus with standard joints in accordance with plans drawn up by the Chemistry Department of the Moscow State University, but when considered in relation with the range and designs of the Schott products, this was a step backwards. The main defect of many of these products was bad design—a consequence of a "paper" approach to this work. Many, though not

all, of the products were quite unsatisfactory for modern laboratory requirements.

The zirconium glass from which the standard-joint ware was being made, though having quite satisfactory chemical stability, had inadequate thermal stability; no standard joints were being manufactured from thermally stable (Pyrex) and molybdenum glasses.

The Ministry of Apparatus Construction was not greatly interested in the requirements of laboratories: it produced far too much apparatus without standard joints and did nothing to encourage the extensive production of new types and the discontinuation of the production of obsolete types.

The total absence of suitable apparatus with standard joints and the persistent demand for such apparatus resulted (1953-1954) in the formation of a Joint Committee of the Institutes of Organic Chemistry and of Heteroorganic Compounds with the object of developing standard glassware with standard joints, the eight members of the committee being D. M. Dubinin, A. V. Kamernitsky, M. I. Rozengart, E. N. Safonova, O. I. Sorokin, O. D. Sterligov (all from the Institute of Organic Chemistry), S. V. Vitt, R. V. Kudryavtsev (from the Institute of Heteroorganic Compounds). The director of the glassblowing workshop, D. M. Dubinin, took a leading part in the work of the committee.

The speaker discussed the general principles which the Committee took as their basis for the design of the most rational pieces of glassware: 1) the use of five sizes of standard joint, 10, 14.5, 19, 29, and 45, this number of joints being essential for the construction of general-purpose laboratory apparatus; 2) the dismemberment of apparatus into individual elements that mutually correspond, so that the maximum number of assemblies can be made - the correspondence here refers to lengths of ends of condensers, adapters, funnels, and thermometers and to the dimensions of still-heads, flask necks, etc.; 3) the suitable use of "through" and "truncated" joints, the former being used in all cases where it is necessary to avoid contact between a pure substance and the joint; 4) maximum reduction in dead space and distance so as to reduce hold-up of substance to a minimum; 5) convenience in use, storage and manufacture.

As a result of the work of the committee "Collection 1" had been prepared. This was entitled "Diagrams of Glassware with Standard Joints" and covered thirty-five types of general-purpose vessels comprising only the most essential apparatus for work with quantities of material of the order of a few thousand grams. The Collection included also diagrams of 170 glass gittings with standard joints. These fittings make it possible to assemble various pieces of apparatus for carrying out reactions, distillations, and filtrations. The products developed by the committee were put to practical test in the laboratories of the Institutes of Organic Chemistry and of Heteroorganic Compounds. The designs were worked out in close collaboration with the glassblowers, account being taken not only of the requirements of chemists, but also of the capabilities of glass blowers of limited experience.

Also, for the first time in the USSR, the Committee and the glassblowing workshop of the Institute of Organic Chemistry developed several types of thermometers with standard joints. At the present time, in order to fulfill the requirements of the Institutes of Organic Chemistry and Heteroorganic Compounds, twenty types of thermometers are being produced: eight for general purposes with 14.5 joints and ranging from 0° to 300°, the length of the lower stem being varied, and twelve short thermometers of the Anschütz type, with upper and lower 14.5 joints and with lower 10 joints, for the measurement of temperatures from 0° to 200°. The speaker then pointed out that, in view of the great desirability of using standard glass apparatus with standard joints in chemical laboratories and the possibilities of organizing bulk production, it was essential to arrange for its production on the industrial scale. In conclusion O. D. Sterligov read the proposals of the Committee. During his presentation of the report, O. D. Sterligov demonstrated glassware produced at the Klin factory in accordance with the designs of the Chemistry Department of the Moscow State University, exhibited the designs given in Schott's catalogue, and showed also samples of the vessels developed by the Joint Committee.

Thirteen people took part in the discussion that followed. All, without exception, expressed approval of and warm support for the initiative of the Committee. The representative of the Kazan Affiliated Institute of the Academy, K. V. Nikonorov, speaking on behalf of Academician A. E. Arbuzov, stated that Kazan chemists were prepared to join in this work. He remarked that the bulk of the ware produced by the Klin and "Victory of Labor" factories for the Moscow State University was imperfect and should be subjected to highly critical examination. An attempt to interfere in the running of the factory with the object of helping it to produce apparatus of more modern design was not very successful. Nikonorov supported the Committee's proposal that apparatus should be made not only from zirconium glass, but also from molybdenum and Pyrex glasses. He made some

criticisms of the designs exhibited at the Conference. He agreed that five different sizes of standard joint were sufficient and he asked the Conference to support the proposal of organizing production of thermometers with standard joints.

Yu. A. Bedov (Institute of Petroleum of the Academy of Sciences) referred to our backwardness as compared with the level of laboratory techniques in foreign countries, who were 25-30 years ahead of us. He urged the Conference to recognize the necessity of approving the activities of the Committee and of drawing all interested organizations into the work of developing standard laboratory glassware in collaboration with the Committee. Bedov proposed that the designs worked out by the Committee should be introduced in the form of standards. He made some criticisms of the work of the Klin factory, stating that the directors of the factory had very little interest in the work of the standard-joint department and had taken no steps to organize production of standard joints from molybdenum and Pyrex glasses, but had confined themselves to zirconium glass. He expressed indignation at the fact that the glassblowers of the standard-joint department should be sometimes transferred to work on the manufacture of Christmas-tree decorations.

E. N. Prilezhaeva (Institute of Organic Chemistry) pointed out that for chemists the question of the standardization of laboratory glassware was a question of raising the productivity of labor in the laboratory. It would be excellent if these beginnings based on the two institutes could be built up on a wider, government scale, bringing in enormous state resources. Our task today, she said, consists in laying the question of the manufacture of standard glassware with standard joints before the government, having first discussed our proposals as thoroughly as possible. E. N. Prilezhaeva proposed that 1) the range of glasses produced should be extended and very strict standards for glasses should be set up; 2) the glassware with standard joints developed by the Committee should be widely discussed; and 3) a proposal should be made to the government that a delegation including scientific workers and foremost workmen of glassblowing workshops and factories should be sent abroad to study foreign experience and practice.

F. S. Titov, a glassblower of the Institute of Organic Chemistry, spoke in support of Yu. A. Bedov's proposal to extend the production of glassware with standard glass joints.

S. D. Levina (Institute of Physical Chemistry of the Academy of Sciences) emphasized that our laboratory techniques show up at their worst with respect to glassware. For physical chemists joints for vacuum apparatus were of very great importance, but such joints were not available from Soviet sources. S. D. Levina stated that it was essential to organize production of fused joints between glasses of different kinds, making use of the experience of the works "Elektrozavod."

Sh. A. Karapetyan (Institute of Heteroorganic Compounds) stated that it was now up to the factories to produce good-quality laboratory glassware with standard joints. In the factories, however, there were quite a few difficulties in the introduction of new processes and designs. The factories must work at maximum productivity, and to achieve this it was necessary to give them the right to turn to new kinds of goods at the request of a group of customers without any red tape that would prevent them from making Christmas-tree decorations instead of the required glassware. It was impossible to introduce rigid standards on the nomenclature of laboratory glassware: a wide range of variants must be provided to meet the needs of different customers. Karapetyan strongly criticized the work of the Chemistry Department of Moscow State University on the development of glassware with standard joints and said that this organization should be brought to account over the question of carrying out such work behind the backs of the general scientific community with the result that all must now suffer from this department's blunders. Karapetyan pointed out that much of the glassware from the Klin works was not suitable for laboratory work and fractionation columns were being cut up in order to obtain Pyrex joints. He revealed the fact that provincial laboratories (e.g., that of the Kaluga Perfume Combine) work with glassware from the Klin factory and take it in wagon-loads, but they can make use of only a small part of the material supplied. This results in a colossal waste of state resources. At the end of his speech Karapetyan stated that, working in collaboration with factories and central organizations, we must seek ways of ensuring the production of laboratory glassware of high quality.

S. V. Vitt (Institute of Heteroorganic Compounds), speaking on behalf of the Committee, informed the Conference about the Committee's immediate tasks, emphasizing the necessity of close contact between factories and customers. The most important task was to get the designs developed into production at the Klin factory.



D. M. Dubinin (Institute of Organic Chemistry) said that the work of the Klin factory must be criticized, but it was necessary also to give the factory some help. The object of the Conference and exhibition of glassware was to take account of the experience on the design of glassware accumulated recently by organic chemists. It was desirable that the small amount of designs provisionally approved should now be produced by the Klin factory. They would have some defects, but when the factory went over to large-scale production and there were more reactions and criticisms it would be easier to introduce improvements in the design of individual components. Dubinin then discussed the production of thermometers with standard joints and stated that production of these thermometers had begun in the glassblowing workshop of the Institute of Organic Chemistry after the Klin thermometer works had refused to make them. In conclusion, Dubinin stated that it would be a complex and difficult task for individual glassblowing workshops to make their own ground joints, but it was not difficult for each chemical glassware factory to organize its own production of standard joints in various kinds of glass. The Klin, Skhodnensk, Moscow, and "Victory of Labor" factories, among others, should do this.

I. E. Bulanov pointed out to the Conference that the factories produced different types of glass but did not use any distinguishing marks, thus creating difficulties in work. He also criticized the products of the Klin factory and stated that it was necessary to produce good laboratory ware with standard joints.

A representative of the Klin factory, P. A. Ornatsky, then came forward and stated that many of the shortcomings in the work of the factory were to be attributed to higher authorities. Thus, the factory was ordered to increase boron-free zirconium glass. The factory would take steps to increase the range of glassware with standard joints, but this ware would be made from zirconium glass. He stated also that in the present year the standard-joint department would again have to turn to the production of Christmas-tree decorations, for the plan for consumer goods was still in force and had even been extended with respect to quantity. The consumer-goods plan was the controlling factor, for there was no target for standard joints. It was quite obvious that Christmas-tree decorations could be produced by any domestic-craft *artel*, and yet they were compelled to make these decorations. In order to increase production of standard joints in the Klin factory it would be necessary to increase the number of workers, since glassblowing work had been insufficiently mechanized in this factory. The Central Organization was not in favor of increase in the number of workers since it would reduce productivity. Moreover, at the present time the places of experienced glassblowers were being taken by young inexperienced workers. In spite of all this, the factory would take all possible steps to organize the production of new types of standard-joint apparatus. P. A. Ornatsky suggested that the technical specifications of the designs developed should be laid down, confirmed by the factory and the Central Organization, and accepted as satisfactory by the customer; the factory could then begin to produce the new glassware. In conclusion, P. A. Ornatsky invited scientific workers of the institutes to take a more active part in the development of various products and to maintain closer liaison with the factory.

A. V. Kamernitsky (Institute of Organic Chemistry) stated that the position in the standard-joint department of the Klin factory was such that, owing to shortage of manpower, the department could satisfy only one-third of the demand for standard-joint apparatus. In this connection the Committee proposed that the standard-joint department should be extended. At that moment 1,500,000 rubles worth of products were lying in this factory and no-one would take it away, and yet the glassware produced to our design never got as far as the stores, but was taken away directly from the workshop. Kamernitsky discussed glass manufacture and stated that it was impossible to reduce the number of types of glass produced, as all of them were required. However, in addition to zirconium glass, industry must produce more molybdenum, Pyrex, quartz, and other glasses, and these glasses must be provided with distinguishing marks.

G. T. Andrianova (Institute of Physical Chemistry) discussed the quality of the products of the Klin factory and, in particular, she stated that, whereas Schott ware had a long life, the products of the Klin works rarely lasted very long. She said that the factories must be given the right to make alterations in design to suit the requirements of their customers. It was essential that one factory in the USSR should be given the task of providing service to scientific, teaching, and works laboratories and of specializing in this sort of work.

P. I. Polyakov (Chemistry Department, Moscow State University) stated that his department approved the initiative of the Committee and considered that it had made a mistake in not organizing a discussion of its designs. He suggested that it was necessary for the Klin factory to make some of the standard joints from Glass 23, Pyrex, molybdenum glass, and other glasses. This was of great importance, since, for example, in his department all apparatus was made either from Glass 23 or from Pyrex, whereas the Klin factory produced standard joints only from Zirconium glass.



In a concluding address, O. D. Sterligov noted that the Conference had approved the work of the Committee and its proposals, and had made various remarks which the Committee would take into account.

The Conference instructed the Joint Committee of the Institutes of Organic Chemistry and of Heteroorganic Compounds, working in collaboration with the Division of Chemical Sciences, to approach the Ministry of Apparatus Construction and the State Technical Commission through the Presidium of the Academy of Sciences, to inform them of the work of the Committee and the Conference and the proposals that had been brought forward, and to describe the abnormal position that had arisen with respect to the provision of laboratory glassware with standard joints for scientific, teaching, and industrial establishments. The Conference requested the Division of Chemical Sciences of the Academy of Sciences to organize the publication of the collection of diagrams of standard-joint glassware prepared by the Committee and to distribute copies to all interested organizations. The Conference considered that it was desirable to give publicity to the work of the Committee and other matters associated with the introduction of laboratory glassware with standard joints in the scientific press. In conclusion the Conference noted the promise of the representative of the Klin factory to produce articles in accordance with designs of the Joint Committee from 1957 onward. The Conference called on all interested organizations to participate in the work of making modern types of glass apparatus available.

O. D. Sterligov  
A. V. Kamernitsky  
O. I. Sorokin

1. The first of the following is a true statement.

2. The second of the following is a true statement.

## GENERAL MEETINGS OF THE DIVISION OF CHEMICAL SCIENCES

SEPTEMBER — NOVEMBER, 1956

A general meeting of the Division of Chemical Sciences was held on September 27-28, 1956, under the chairmanship of Academician M. M. Dubinin. I. V. Tananaev, Corr. Mem. Acad. Sci. USSR, read a paper on "Chemistry of Metal Ferrocyanides and their Practical Importance." He remarked that metal ferrocyanides comprise a very extensive but little studied class of compounds. One basis of their use in technology and analytical chemistry is their low solubility. However, the scales on which they are applied are limited owing to their great variability in chemical composition due to the tendency to form mixed salts, the theoretical aspects of which process have as yet been inadequately studied. The investigations directed by I. V. Tananaev in the Institute of General and Inorganic Chemistry of the Academy have revealed some of the laws characterizing the formation of mixed ferrocyanides of alkali metals (lithium, sodium, potassium, rubidium, cesium, and univalent thallium), on the one hand, and such "heavy" metals as magnesium, calcium, strontium, zinc, cadmium, yttrium, lanthanum, cerium, neodymium, gallium, indium, zirconium, lead, manganese, iron, cobalt, nickel, thorium, and uranium, on the other.

Many new compounds were isolated and, moreover, it was shown that in certain cases it was possible to predict the course of reaction in such systems. It was shown that all the diversity of forms of interaction between alkali-metal ferrocyanides and the usual heavy-metal salts could be referred to four types of solubility diagrams with the aid of which questions of the formation of structure of ferrocyanides could be resolved. An examination of all the data on the chemical behavior of mixed ferrocyanides revealed their multinuclear structure and the difference in the strengths of the bonds formed in them by alkali and heavy metals. A concept was formulated concerning the zonal structure of the outer cationic sphere of complex ferrocyanides. Owing to the difference in the conditions required for ion exchange of the two outer-sphere metals, so characteristic and strongly marked in mixed ferrocyanides, they may be regarded as inorganic analogs of ion-exchange resins. I. V. Tananaev proposed a method for the determination of the exchange capacity of mixed ferrocyanides consisting in a study of the exchange reaction between alkali-metal ions and normal ferrocyanides of heavy metals. In conclusion, he remarked that the ion-exchange properties of mixed ferrocyanides, their solubility, and their multinuclear structure open up possibilities of effecting a considerable number of new processes, including the extraction of very small amounts of alkali and rare metals from solution, the separation of certain difficultly separable pairs of metals (zirconium-hafnium, rubidium-cesium, individual rare-earth metals), and, finally, the analytical determination of most of the elements.

Contributions to the discussion on papers were made by I. P. Alimarin, V. I. Spitsyn, A. V. Novoselova, A. A. Grinberg, B. P. Nikolsky, M. M. Dubinin, and others.

In his paper on "Metal Chemistry and Some of its Problems," Dr. I. I. Kornilov described the general task of metal chemistry as "study of the interaction of metallic elements among themselves and also with metalloids when the latter form solutions or compounds having bonds of metallic character." He remarked that elements that are similar in chemical properties have no tendency to form metallic compounds, but form continuous solid solutions: for example, chromium and molybdenum, nickel and cobalt, titanium and zirconium, silicon and germanium. However, as the difference in chemical properties of the elements increases, there is an increase in the tendency to form metallic compounds, the composition and structure of which depend on the positions of the elements in the periodic system. The speaker indicated the most important lines of development in metal chemistry; these included 1) further development of the theory of the formation of metallic solutions and compounds, bond strengths being studied by the methods of crystal chemistry, thermochemistry, and radiochemistry; 2) study of the compositions and structures of simple and complex metallic compounds and their

solid solutions in multicomponent systems by the method of chemical and selective separation from alloys of complex structure. The speaker expressed the opinion that fundamental data on bond strengths in metallic solutions and compounds might find application in the solution of a practical problem: the production of alloys of predetermined properties.

Contributions to the discussion on this paper were made by N. A. Torotsov, V. I. Mikheeva and M. M. Dubinin.

D. N. Kursanov, Corr. Mem. Acad. Sci. USSR, read a paper on the "Hydrogen-exchange Reaction of Cyclopentadiene." He described an investigation on the mobility of hydrogen atoms in this reaction in presence of the alkaline catalyst N,N'-dimethylpyridonimine. It was shown that all six hydrogen atoms of cyclopentadiene would undergo hydrogen exchange with deuterium oxide in dioxane solution under very mild conditions. In this reaction the hydrogen atoms of the methylene group show no special properties. D. N. Kursanov described a reaction mechanism that had been confirmed experimentally. Study of the exchange propensity of ferrocene showed that this substance did not undergo hydrogen exchange to any appreciable extent. The speaker stated that, if the bonding of iron with the cyclopentadienyl were purely ionic, this phenomenon could not occur.

Contributions to the discussion were made by A. I. Shatenshtein, A. N. Frumkin, Ya. K. Syrkin, M. M. Shemyakin and M. M. Dubinin.

Dr. Ya. L. Goldfarb gave a paper on the "Synthesis of Aliphatic Compounds from Thiophene and its Homologs." He stated that in recent years in the US there had been practical application of the method of synthesizing thiophene from a C<sub>4</sub> petroleum fraction and sulfur or sulfur dioxide. In the USSR the source of thiophene and particularly of its homologs was the Povolzhya shale tar. Great interest is presented by the synthesis from this raw material of aliphatic compounds that are not readily available by other synthetic methods. In this process thiophene forms an intermediate link, opening the possibility of building up chains of various structures and length and of introducing the necessary functional groups. This is brought about by reductive desulfurization with the aid of Raney nickel. By this method the author obtained higher alcohols, glycols, acids, hydroxy acids, amino acids, etc. Goldfarb pointed out that some of these compounds may find application as components of fuels and oils, as starting materials for polycondensation processes, etc. However, for this it is necessary that yields should be increased and further improvement should be made in the catalyst.

Contributions to the discussion were made by M. I. Kabachnik, I. L. Knunyants, N. I. Shuilkin, M. M. Shemyakin and B. A. Arbuzov.

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A general meeting of the Division was held on October 25-26, 1956, under the chairmanship of Academician M. M. Dubinin. Academician S. I. Volfkovich read a paper on "Problems of the Chemistry and Technology of Phosphorus Fertilizers." He remarked that, in spite of a century's experience and the large scale on which phosphorus fertilizers were produced, their chemistry and technology were in a state of continuous progress associated with considerable qualitative changes. Some new scientific and technical problems had arisen in connection with the progress of biological sciences, particularly as a result of the use of radioactive and stable isotopes. As a result of physicochemical analysis and crystal-optical and x-ray-structural studies of phosphates, investigators had been able to obtain a more profound concept of the mineralogical composition, structure, and origins of apatites and phosphorites. Greater attention had been paid to the utilization of fluorine and various rare elements, particularly lanthanides and uranium entering into the composition of certain natural phosphates. The speaker emphasized that the treatment of phosphates with nitric acid was becoming more and more general owing to the almost complete coordinated utilization of the reactants and the twofold utilization of the nitric acid: for decomposition of the phosphate and as a component of a nitrate fertilizer. The main differences between different schemes for the nitric acid treatment of phosphates consist in the methods of binding and separating calcium and of obtaining simple and complex fertilizers. We have recently started production of double and triple fertilizers by decomposition of phosphates with nitric acid or with a mixture of nitric and sulfuric acids without separation of calcium nitrate or sulfate and with subsequent neutralization of the resulting intermediary with ammonia; also, the important problem of replacing sulfuric acid with carbon dioxide has been solved.

In the USSR a works for the treatment of phosphates in accordance with the three schemes that we have developed has been set up and is in operation. Soviet industry is envisaging considerable development of the nitric acid treatment of phosphates. The hydrothermal treatment of phosphates had been studied both on synthetic preparations (fluoro- and hydroxy-apatites) and on various natural phosphates, particularly on Khibin apatite concentrate containing nepheline. The effects of impurities in or additives to the phosphates, such as silica, alumina, soda, lime, magnesia, clay, and nepheline, were studied. The most effective additive was silica (sand, and then nepheline; the latter considerably lowers the fusibility of the charge). The presence of magnesia has a favorable effect on the passage of phosphate into the citrate-soluble form. When limestone is added to some low-melting phosphorites, not only is the melting point of the charge raised, but the phosphate passes into the citrate-soluble form. The rate of defluorination is proportional to the rate of diffusion of the fluoride ion from the center of the crystal or fused layer of apatite to the surface. In order to find the relationship between physiological efficiency, composition, and structure of phosphate compounds, a series of silicophosphates falling in various fields of the  $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$  diagram was synthesized. The resulting preparations were investigated chemically, microscopically, and by x-rays. Defluorinated phosphates not containing combined silica readily pass into hydroxyapatite by reaction with water. In silicophosphates, such a change is either very slow or does not occur at all. Academician Volkovich stated that the preparation of fused magnesian phosphates from charges consisting of phosphate ores, natural magnesium-containing silicates, and carbonates makes it possible to obtain magnesia-phosphate fertilizers in shaft, reverberatory, and electric furnaces. The products contain 17-20%  $\text{P}_2\text{O}_5$  and 12-17%  $\text{MgO}$ . The process of interaction between natural phosphate and magnesium sulfate, which has been recently realized in the German Democratic Republic, is of interest. By reaction of metaphosphoric acid vapor with limestone or phosphate, a highly concentrated phosphate fertilizer can be prepared - calcium metaphosphate containing up to 66%  $\text{P}_2\text{O}_5$  (the method was first proposed in the USSR by E. V. Britske). An interesting variant is the oxidation of phosphorus with water vapor or liquid water with formation of elementary hydrogen, which has been studied in the USSR and other countries. The hydrogen obtained may be combined with nitrogen to give synthetic ammonia, from which, by reaction with phosphoric acid, ammonium phosphates can readily be obtained. There arises, therefore, the interesting problem of combining two large-scale chemical industries - phosphorus and phosphoric acid, on the one hand, and synthesis of ammonia, on the other. By the electrothermal treatment of phosphates we may obtain not only  $\text{P}_2\text{O}_5$  and concentrated acids, but also "superconcentrated" complex fertilizers: ammonium metaphosphates containing up to 73.2%  $\text{P}_2\text{O}_5$  and 17.5%  $\text{NH}_3$  and potassium metaphosphate containing 53-54%  $\text{P}_2\text{O}_5$  and about 38%  $\text{K}_2\text{O}$ .

Contributions to the discussion on the paper were made by S. Z. Roginsky, A. F. Kapustinsky, and others.

V. V. Hlarionov, Candidate of Chemical Sciences (Institute of Fertilizers and Insectofungicides of the Ministry of Chemical Industry), reported an investigation of the phosphorus-sulfur and sulfur-selenium systems by the method of physicochemical analysis. By the author's method of temperature reversions, decomposition curves were determined for solid solutions, and thermographic, x-ray, and other investigations were also carried out. Some unstable compounds were studied, and the vapor pressures of stable sulfides were determined, which allowed their state in the melts to be determined and the resulting data to be utilized for technological purposes. The results give reason to suppose that it is possible to purify sulfur from selenium and make an approach to a technical scheme of purifying sulfur obtained by the treatment of sulfide ores by rectificational condensation.

Contributions to the discussion were made by A. F. Kapustinsky, S. Z. Roginsky, N. N. Semenov, and M. M. Dubinin.

In a paper on the "Properties and Structure of Beryllium Fluoride Compounds," A. V. Novoselova, Corr. Mem. Acad. Sci. USSR, reported her investigations on the phase diagrams of systems containing beryllium fluoride and fluorides of various metals, which make it possible to find the conditions for the formation of various complex beryllium fluorides and to determine some of their properties. A modification of  $\text{BeF}_2$  similar to quartz was found. Thermal and x-ray investigation of modifications of beryllium fluoride indicated the existence of an analogy between crystalline beryllium fluoride and silica. The phase diagrams of the systems  $\text{MF}-\text{BeF}_2-\text{H}_2\text{O}$  ( $\text{M}$  = alkali metal) were investigated by the solubility method and by x-ray phase analysis; the existence of  $\text{M}_2\text{BeF}_4$ ,  $\text{MBeF}_3$ , and  $\text{MBe}_2\text{F}_5$  was established.

A. V. Novoselova remarked that the types of phase diagrams of silicate systems and model fluoride systems were basically similar, but there were differences, so that it was not possible to pass by quantitative recalculation from the invariant points of fluoride systems to the corresponding points of silicate systems. It is of



scientific and practical interest to investigate glasses containing beryllium fluoride compounds, for they are distinguished by extremely low refractive indices and transmittance for radiation over a wide range of frequencies; also, fluoride glasses may serve as models for silicate glasses.

Contributions to the discussion were made by V. I. Spitsyn, B. V. Nekrasov, S. Z. Roginsky and M. M. Dubinin.

I. E. Starik, *Corr. Mem. Acad. Sci. USSR*, read a paper on "Form in which Radioelements occur in Crystalline Substances." He pointed out that the difference between these radioelements and the usual elements consist, apart from their radioactivity, in their formation in the crystal after the crystal itself has been formed and in their difference in chemical and crystal-chemical properties from the parent substances forming part of the crystal lattice. The study of this matter can be most successfully carried out on natural formations, i.e., radioactive minerals, since we then have radioactive equilibrium. However, owing to the extremely small amounts of the radioelements formed, the usual methods of investigation have been found to be inapplicable. All results on the form of existence of radioelements (decay products) in crystalline lattices has been obtained indirectly - by study of the emission of emanation and comparative leachability. It was shown that the emission of the minerals investigated was not a surface process, but a volume process. Since diffusion in the crystal lattice itself is almost absent, it is natural to suppose that it occurs through dislocations in the crystal - along networks of capillaries existing in the crystal. Work with radium isotopes showed that the percentage leachability in a neutral medium is generally considerably lower than the emanation coefficient, but when the solution contains other cations the leachability rises sharply; when a sufficient concentration of bivalent metal ions is present the leachability and emanation coefficient become almost equal. In all investigated cases it was shown that in weakly acid, neutral, or weakly alkaline media radium isotopes are leached out preferentially as compared with uranium. When a sufficiently high acidity is attained, dissolution occurs and radium and uranium pass into solution in equilibrium amounts. Two processes must therefore be distinguished in the passage of radioelements from a mineral to a liquid phase: leaching and dissolution. Leaching is the passage of any element from the mineral without any breakdown of the crystal lattice. Dissolution is the passage into solution of all elements composing the mineral. On the basis of these concepts a theory is proposed for the formation of natural waters rich in radioelements.

Contributions to the discussion were made by I. P. Alimarin, S. Z. Roginsky, M. M. Dubinin and others.

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A general meeting of the Division was held on November 22-23, 1956, under the chairmanship of Academician M. M. Dubinin. B. V. Deryagin, *Corr. Mem. Acad. Sci. USSR*, and Dr. N. A. Krotkova presented a paper on the "Part Played by Electrical and Molecular Phenomena in the Adhesion of Polymer Films." The authors stated that one fundamental problem in the study of surface phenomena is the investigation of processes accompanying the formation of new interfaces, e.g., during mechanical treatments. However, the examination of such processes on the basis of the thermodynamics of surface phenomena, as is often done, is not only inadequate, but can lead to erroneous conclusions. Only a kinetic approach, based on an examination of the mechanism of the process, can lead to the development of a theory of these phenomena. In the stripping of polymer films from metals, glasses, and also polymers, electric discharges are observed, which indicates the formation of high potential differences. Theory enables us to calculate, on the basis of the most probable values of charge density in the double electrical layer, the work expended per unit area of film in rapid stripping. This quantity is generally higher by a factor of several powers of ten than the work required stripping against van der Waals and valence forces.

Hence, in the interpretation of the work of adhesional stripping of polymer films, there is no sense in considering the contribution made by these last forces, as has generally been done. The work required for the stripping of polymer films as measured directly under various conditions (rate of stripping, pressure and kind of surrounding gas) is quantitatively very close to the work that would be required to separate the oppositely charged components of the double layer, which confirms the electrical theory of adhesion developed by the authors. For the quantitative verification of the theory use was made of measurements of energies and velocities of fast electrons, the emission of which in the formation of new interfaces was first detected and investigated by the authors. These measurements showed that in the stripping of film in a vacuum the potential differences formed (about

10 kv) were exactly of the same order as those required to explain the value obtained for the amount of work expended in stripping. An analogous phenomenon of emission of fast electrons (up to 150 kv) was found in the mechanical destruction of crystals in a vacuum. In the cohesive destruction of amorphous substances electrical phenomena are absent. In this case, high work of formation of new surfaces may be explained by entropy effects in the disentanglement of polymer chains accompanying the formation of new rupture surfaces. The same effect arises also in the adhesional separation of two copolymers, previously in contact.

Contributions to the discussion were made by P. A. Rebinder, V. A. Kargin, and M. M. Dubinin.

A paper by Dr. A. V. Kiselev was devoted to the adsorption energy of hydrocarbons. It covered work done in 1956 on the determination of adsorption isotherms and differential heats of adsorption, on the thermodynamics of adsorption, and on theoretical calculations of the energies of adsorption forces for a series of pure hydrocarbons of various structures adsorbed on graphitic and silica-gel adsorbents. With the aid of a sensitive autographic adsorption calorimeter with automatically controlled constant heat exchange and of an adsorption apparatus with a vacuum microburet for liquids, the author was able to make a detailed study of the relation between differential heats of adsorption of various hydrocarbon vapors and the surface coverage of untreated and graphitized carbon blacks. This made it possible to investigate in detail the adsorption equilibria in the uni- and multi-molecular regions and to determine standard thermodynamic characteristics of the adsorption of hydrocarbons and their dependence on the molecular structure of the latter, i.e., to calculate their adsorption equilibria. This made it possible also to compare theoretically calculated values of energies of adsorption forces with calorimetrically determined heats of adsorption. Results of the theoretical calculation of adsorption energy on graphite were compared with differential heats of adsorption determined in the calorimeter for graphitized carbons having fairly homogeneous surfaces. In all cases in which it was possible to make such comparisons it was found that these values were in close agreement. The theory developed, therefore, makes it possible to shorten the experimental work considerably and to predict, with satisfactory accuracy, the adsorption energies of many complex molecules on the basis of their structures. In parallel with this work on graphitic adsorbents, which was carried out in the Sorption Laboratory of the Institute of Physical Chemistry of the Academy of Sciences of the USSR, work on heats of adsorption of hydrocarbons on silica gels of various structures and the extent of their surface hydration was going on in the Adsorption Laboratory of the M. V. Lomonosov State University, Moscow. In this case physical interactions, which play a leading part in the adsorption of hydrocarbons on graphites, are very much weaker, but in the adsorption of unsaturated and aromatic hydrocarbons they are accompanied by more intense interactions with formation of molecular complexes ( $\pi$ -complexes) of an acid-base type.

Investigation of the heats of adsorption of the vapors of normal paraffins on graphitized blacks and silica gels showed that their adsorption energies are additive functions of the adsorption energies of the separate structural units of the hydrocarbon molecules and are much greater for graphitic adsorbents than for silica gels. The adsorption energies of isoparaffins are much less than those of normal paraffins.

In the case of graphitic adsorbents, the adsorption energy of paraffins is greater than that of aromatic hydrocarbons with the same number of carbon atoms in the molecule. In the case of silica gels having a hydrated surface, as a result of the superposition of the interaction of the  $\pi$ -electrons of aromatic compounds with the hydroxyl of silicic acid, the heat of adsorption of aromatic hydrocarbons is considerably greater than that of saturated hydrocarbons. In this relation, with dehydration of the silica gel surface the heat of adsorption of benzene is greatly reduced, while the heat of adsorption of saturation hydrocarbons scarcely changes.

Contributions to the discussion were made by Ya. K. Syrkin, A. N. Frumkin, A. N. Terenin, V. K. Semchenko, and M. M. Dubinin.

A paper on the "Catalytic Cyclization of Paraffins with Formation of Five-membered Rings" was presented by Academician B. A. Kazansky and A. L. Liberman, Cand. Chem. Sci. The authors stated that, in presence of platinized charcoal at 300° or chromium oxide at 500-550°, paraffins can be converted to a greater or less extent into aromatic hydrocarbons with elimination of hydrogen. In presence of platinized charcoal this reaction proceeds with intermediate formation of cyclohexane hydrocarbons, but, as the authors and their coworkers established in 1953-54, with long contact with this catalyst at 310° cyclopentane hydrocarbons can also be formed in amount exceeding that of the aromatic hydrocarbons.

Thus, n-heptane gives ethylcyclopentane and 1,2-dimethylcyclopentane; n-octane gives propylcyclopentane and 1-ethyl-2-methylcyclopentane, as would be expected from the structures of the original paraffins.

2,2,4-Trimethylpentane can form and, in fact, does form a single homolog of cyclopentane, 1,1,3-trimethylcyclopentane; 3-ethylpentane gives ethylcyclopentane. Both these hydrocarbons can be isolated from the reaction mixture by fractional distillation. 2,2,3- and 2,3,3-Trimethylpentanes give 1,1,2-trimethylcyclopentane, as can be proved spectroscopically. The yields of cyclic hydrocarbons depend greatly on the nature and structure of the original paraffins, on the time of contact with the catalyst, and on the amount of work the catalyst has done. Under the conditions cited n-pentane cyclizes only very slightly, and although n-heptane and n-octane cyclize to an appreciable extent, the yield is still too low for the cyclization products to be readily isolated. The above highly branched hydrocarbons cyclize to a much greater extent; thus with fresh catalyst 2,2,4-trimethylpentane gives a 25-30% yield of 1,1,3-trimethylcyclopentane. However, the catalyst gradually loses its activity and becomes stabilized, when it gives yields of cyclic hydrocarbons of 6-10% from paraffins of various structures. There is a linear relation between the rate of cyclization of 2,2,4-trimethylpentane and the time of contact. This reaction is applicable not only to paraffins, but can be carried out also with benzene homologs having a side chain containing not less than three carbon atoms.

Contributions to the discussion were made by S. Z. Roginsky, N. I. Shuikin, M. M. Dubinin, and others.

Dr. V. I. Ivanov read a paper on the "Structure of the Cellulose Molecule and its Breakdown." He reminded the audience that the concept of the cellulose molecule as a chain containing about 3000 D-glucopyranose residues united through 1,4  $\beta$ -glucoside links was established in 1936 by more than a century's work by investigators in different fields. The first objections to this structure were brought forward in 1941 by O. P. Golova and the present author, who showed that the degree of polymerization of cellulose is not 3,000, but about 10,000.

Kinetic, polarimetric, static, and chemical methods of investigating the structure of cellulose established that 99-99.9% of the links between glucose residues are 1,4-linkages. The speaker stated the basis for the view that weaker glucosidic linkages are present, critically analyzed the existing data on their chemical nature, and also introduced necessary corrections into existing concepts of the properties of oxycelluloses and the chemistry of their breakdown. On the basis of experimental data the thermal stability of the cellulose molecule was estimated and it was shown that the main direction in which thermal degradation proceeded resulted finally in the formation of levoglucosan, a product of considerable practical importance for the national economy.

Contributions to the discussion were made by N. I. Nikitin, Z. A. Rogovin, N. V. Mikhailov, M. M. Dubinin, and others.

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Division of Chemical Sciences

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TABLE OF CONTENTS

	Page	Russ. Page
1. Mendeleev and the Present State of Development of His Ideas. <u>A. F. Kapustinsky</u> , . . .	137	129
2. Congratulations to Valentin Alekseevich Kargin. . . . .	145	138
Inorganic and Analytical Chemistry		
3. Systems Containing Hydrogen Peroxide at High Concentration. Communication 13. Properties of Peroxy Compounds of Zinc. <u>S. Z. Makarov and L. V. Ladeinova</u> , . . .	147	139
Physical Chemistry		
4. Mechanism of the Dissociation of a Diatomic Molecule on Adsorption of the Surface of a Semiconductor. <u>F. F. Volkenshtein</u> , . . . . .	151	143
5. Dehydrogenation of Butane-Butene Mixtures Investigated with the Aid of C <sup>14</sup> . <u>A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isagulyants, A. P. Shecheglova and E. I. Popov</u> , . . . . .	167	157
6. Preparation of 1,6-Hexanediamine by Hydrogenation of Adiponitrile over a Nickel Catalyst Under Flow Conditions. <u>L. Kh. Freidlina, A. A. Balandin, K. G. Rudneva and T. A. Sladkova</u> , . . . . .	177	166
7. Kinetics and Chemistry of the Polycondensation of $\alpha$ -Amino Esters. Communication 2. Kinetics of the Polycondensation of Glycine Ethyl Ester. <u>Yu. I. Khurgin, K. T. Poroshin and T. D. Kozarenko</u> , . . . . .	185	174
Organic and Biological Chemistry		
8. Ethylphosphonous Esters and Some of Their Reactions. Communication 7. Mixed Anhydrides of Ethylphosphonous Acid and Dialkyl Hydrogen Phosphites and the Mixed Anhydride of Ethylphosphonous Acid and Isopropyl Hydrogen Ethylphosphonite. Diethyl Ethylphosphonodithioite. <u>B. A. Arbuzov, N. I. Rizpolozhensky and M. A. Zvereva</u> , . . . . .	189	179
9. Reaction of Mercuric Acetate with Xanthic Esters. <u>R. Kh. Freidlina and E. Ts. Chukovskaya</u> , . . . . .	197	187
10. 2-Chloroethyl Esters of Some Phosphorus Acids. <u>E. L. Gefter and M. I. Kabachnik</u> , . . .	205	194
11. Some Regularities Observed in the Chlorination of Organosilicon Compounds. <u>V. F. Mironov and V. A. Ponomarenko</u> , . . . . .	211	199
12. Synthesis of Steroids and Related Compounds. Communication 39. Steroid Analogs not Containing Ring B. <u>I. N. Nazarov and S. I. Zavyalov</u> , . . . . .	219	207
13. Bromomethylation of Aromatic Hydrocarbons. <u>I. N. Nazarov and A. V. Semenovskiy</u> , . .	225	212

# TABLE OF CONTENTS (continued)

	Page	Russ. Page
14. Action of Raney Nickel on Ethers of the Thiophene Series. <u>Ya. L. Goldfarb and P. A. Konstantinov.</u> . . . . .	229	217
15. Oligomerization. Communication 2. Reaction of some Vinyl Ethers with Carbon Tetrachloride in Presence of Various Initiators. <u>A. V. Bogdanova and M. F. Shostakovsky.</u> . . . . .	235	224
Brief Communications		
16. Energy of Adsorption Forces and Heat of Adsorption of Simple Molecules on Graphite. <u>N. N. Avgul and A. V. Kiselev.</u> . . . . .	241	230
17. Debye Dispersion of Adsorbed Water at Low Temperatures. <u>I. V. Zhilenkov.</u> . . . . .	245	232
18. Electron Charges of Bonds in Ethylene, Allene and Benzene. <u>G. V. Bykov.</u> . . . . .	249	235
19. Polymerization of Acrylonitrile in Presence of Tributylborane. <u>G. S. Kolesnikov and L. S. Fedorova.</u> . . . . .	251	236
20. Hydrodimerization of Acrylonitrile. <u>I. L. Knunyants and N. S. Vyazankin.</u> . . . . .	253	238
Current Events		
21. International Congress on Catalysis in Philadelphia. <u>N. I. Shulkin.</u> . . . . .	257	241
22. Conference on the Standardization of Laboratory Glassware. . . . .	261	244
23. General Meetings of the Division of Chemical Sciences. September-November, 1956 . .	267	248





